1967

Kinetics of the Catalytic Autoxidation of Erythritol in Basic Solution.

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SCOTT, Kenneth Charles, 1940-

KINETICS OF THE CATALYTIC AUTOXIDATION OF ERYTHRITOL IN BASIC SOLUTION.

Louisiana State University and Agricultural and Mechanical College, Ph.D., 1967
Engineering, chemical

University Microfilms, Inc., Ann Arbor, Michigan

KINETICS OF THE CATALYTIC AUTOXIDATION OF ERYTHRITOL IN BASIC SOLUTION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by
Kenneth Charles Scott
B. S., University of Missouri Schools of Mines and Metallurgy, 1962
M. S., Louisiana State University, 1964
January, 1967

ACKNOWLEDGEMENTS

The author expresses his sincerest appreciation to Dr. Frank R. Groves, Jr., Associate Professor of Chemical Engineering at Louisiana State University for his able direction and assistance during this investigation.

The financial assistance granted to the author by the Ethyl Corporation is recognized and appreciated. Thanks are also due to the Dr. Charles E. Coates Memorial Fund, donated by George H. Coates, for financial assistance for preparation of the manuscript.

A special word of appreciation is also given to my wife, Paula, for her understanding during the research effort.

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ABSTRACT

The kinetics of the catalytic liquid phase autoxidation of erythritol was studied in a gas sparged reactor. The reaction will not proceed to any measurable extent in an acid medium or in the absence of either ferric chloride catalyst or oxygen.

The major products formed were glyceric, glycolic and formic acids. Product analysis was made by temperature programmed gas chromatography of the trimethylsilyl ethers of the acids and the erythritol. The method was found to work quantitatively for other related acids and alcohols. The erythritol concentration was also determined by the periodic acid method, the acids being removed from solution by ion exchange columns.

A rate study was made of the significant reaction variables. Precautions were taken to ensure that mass transfer effects were minimized. Under the conditions of the tests, the rate was independent of the gas sparging rate, and the temperature coefficient was of a value expected from kinetic effects.

The rate curves usually contained three regions; (1) an initial unsteady state period in which the rate was high, (2) an intermediate period in which the rate was nearly first order with respect to erythritol concentration and (3) a later period in which there appeared to be a "catalyst poisoning effect".

In region (2) the rate was found to be nearly first order with respect to the total catalyst concentration, and at low erythritol concentrations first order with respect to the erythritol concentration. In the range of concentrations studied the rate was nearly independent of hydroxyl ion concentration.

The rate data was explained by a mechanism which included the formation of two chelate compounds between erythritol and the ferric ion, one oxidizable and one essentially unoxidizable. The derived rate expression was:

$$\frac{-d[C_E]}{d\theta} = \frac{k' [Fe]_o [H_4E]}{A + K_2[H_4E]}$$

where: $[Fe]_o$ = initial ferric ion concentration

$[H_4E]$ = erythritol concentration

$$A = 1 + k_2 \frac{[HGo]}{[H_4E]} + k_3 \frac{[HGe]}{[H_4E]}$$

[HGo] = concentration of glycolic acid

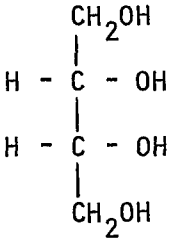
[HGe] = concentration of glyceric acid

The "catalyst poisoning effect" is accounted for by the A term and is due to the chelate compounds formed between the ferric ion and the acid products. Tests showed that significant quantitites of glyceric acid would totally inhibit the reaction.

CHAPTER I

INTRODUCTION

This dissertation gives the results of a kinetic study of the autoxidation of meso-erythritol, a four carbon polyhydric alcohol with the following structure.



The main reason for the interest in the reaction is due to the similarity between erythritol and mannitol. Mannitol is a six carbon homolog of erythritol and is called a "sugar alcohol" because of it's similarity to monosaccharides. Compounds similar to mannitol are found in the waste streams of sugar and paper mills. These alcohols are not appreciably oxidized during waste treatment by the methods designed primarily for sugar compounds, resulting in a large B. O. D. (Biological Oxygen Demand) value for the streams.

Traube[1] found that when mannitol is added to an alkaline solution containing ferric ions, ferric hydroxide would not precipitate. He suggested the behavior was due to the formation of a mannitol-iron(III)

complex and later found that the mannitol would oxidize in the presence of molecular oxygen.

The reaction is also interesting because of the possibility of the production of useful products. Mannitol is relatively cheap and the possible acid products such as arabonic, erythronic, glyceric and glycolic acid are expensive.

There has been little work on this particular type of autoxidation. A survey of previous investigations that are pertinent to this study are discussed in Chapter II.

In Chapter III, related mechanisms are discussed and the background for some of the suggested reactions are given.

Chapter IV contains information about the equipment used and a description of the analytical methods developed. The methods developed for erythritol and its reaction products are shown to be applicable to related acids and alcohols.

The results of the kinetic tests are presented in Chapter V and the postulated mechanism in Chapter VI.

Chapter VII contains a summary of the results and suggestions for further investigations.

Literature Cited

1. Traube, Wilhem and Kuhbier, Fritz, "Complex Ferric Compounds of Pohydydric Alcohols", Ber. 65B, 187-90 (1932).

CHAPTER II

EARLIER INVESTIGATIONS

There has been very little work on the oxidation of erythritol. Studies that involve mechanisms similar to the one being studied, but not specifically of erythritol or mannitol are included in Chapter III.

A. Fenton[5]

The earliest investigation of the oxidation of erythritol was by Fenton. Erythritol, water and ferrous sulphate were mixed together and hydrogen peroxide was added slowly. The aldehyde of erythritol, erythrose, was formed, as evidenced by the precipitation of erythrosozone upon the addition of phenylhydrazine acetate. The same procedure was followed with ethylene glycol, mannitol, dulicitol and sorbitol with the production of the corresponding aldehydes. Monohydric alcohols would not react under the same conditions. The same products were also obtained with the reaction was carried out in the presence of sunlight and atmospheric oxygen. The reaction would not proceed in the absence of sunlight nor would it proceed in the presence of the ferric ion. This suggests that the reaction probably involves a hydroxyl radical, produced by the hydrogen peroxide, and might involve a mechanism similar to the one shown below.

$$Fe^{++} + H_2O_2 \rightleftarrows HO^{\cdot} + OH^{-} + Fe^{+++} \qquad 2.1$$

$$Fe^{+++} + H_4E \rightleftarrows Fe\ (H_2E)^{-1} \qquad 2.2$$

$$Fe\ (H_2E)^{-1} + \ \cdot OH \rightarrow Fe\ (HE)^{-1} \qquad 2.3$$

$$Fe\ (HE)^{-1} \rightarrow \text{products} \qquad 2.4$$

The autoxidation of olefins[1] and hydrocarbons[6,9] also supposedly occurs by a radical mechanism whereas the autoxidation of sugars[2] occurs through ionic intermediates.

B. Küchlin[7]

Küchlin also studied the oxidation of erythritol by hydrogen peroxide in the presence of Fe^{++} salts. Treatment of the oxidation products with semicarbazide gave a semicarbazone with a M.P. of 222°C, indicating that the final product contained erythrose and unreacted erythritol.

C. Traube and Kuhbier[12,13]

Traube and Kuhbier found that ferric hydroxide did not precipitate when mannitol was added to the alkaline solution containing the ferric ion. The autoxidation of the ferric-mannitol and the ferric-erythritol complex was studied. The results obtained from the autoxidation of erythritol are summarized in Table (II-1). Traces of hydrogen peroxide were detected during the oxidation. One of the products formed during

Table (II-1)

Results of Autoxidation of Erythritol by Traube and Kuhbier[13]

Experiment Number	Original Erythritol Gram Moles	CM^3 6.2% Ferric Chloride	Temperature °C	Reaction Time (Hours)	Gram Moles Carbon Dioxide	Gram Moles Formic Acid	Gram Moles Erythronic Acid	Gram Moles Erythritol Remaining	Gram Moles Oxygen Absorbed
18	.01635	6.0	30.0	48	.000705	.00333	-	-	.0226
19	.0246	2.5	37.0	24	.00405	-	-	.00573	.01969
20	.01635	2.5	37.0	48	.00661	.0144	.00344	Traces	.0295
21	.01635	2.5	37.0	60	.00406	.01261	.00283	Traces	.0236
22	.01635	2.5	37.0	60	.00814	.00903	-	Traces	.0299

the oxidation of mannitol was oxalic acid. The precipitated product formed when barium hydroxide was added to the erythritol-iron(III) complex had the following structure.

$$(C_4H_7O_5)_2\ Ba \cdot 2H_2O$$

D. Salley[10,11]

Salley studied the autoxidation of mannitol in the presence of ferric chloride because of its similarity to cellulose. The principal aim of the work was to determine a way to inhibit the oxidation. The rate of oxidation was studied by following the rate of oxygen uptake. The curve obtained of oxygen uptake versus time was auto-accelerating in nature until a fairly constant rate was obtained.

An induction period was observed at lower iron and alkali concentrations which lasted from ten minutes to one hour, during which no oxygen was absorbed. The following results were obtained: (1) The reaction rate increases with mannitol concentration until about .1M, higher concentrations do not increase the rate proportionally. (2) The reaction rate increases with temperature. A temperature coefficient, k_{35}/k_{25}, of approximately 5.0 was obtained. (3) The rate increases nearly proportionally with increased sodium hydroxide concentration. (4) The rate is increased by increasing the catalyst concentration but the efficiency drops off at high catalyst concentrations. (5) The rate of oxidation is accelerated by light. (6) The oxidation does not occur by a chain mechanism. The quantum yield revealed that

only one molecule of oxygen reacts for every 25 or 30 quanta of light absorbed by the solution. (7) Known inhibitors of chain reactions do not affect the rate. (8) The presence of hydrogen peroxide accelerates the rate.

Salley concluded that some sort of oxidative mechanism involving free hydroxyl radicals was present. The oxidation of mannitol was also studied in the presence of photosensitized hydrogen peroxide. Results from this study also ruled out a long chain mechanism.

E. Callejas[3] and Milian[8]

Callejas found that an induction period in the autoxidation of mannitol in the presence of cupric ion was present at temperatures below 50°C. Various metals were tested to determine catalytic ability. Following is a summary of the results.

Metal Ion	Complex Formed?	Catalyze Autoxidation?
Fe^{+++}	Yes	Yes
Cu^{++}	Yes	Yes
Co^{+++}	Yes	Yes
Bi^{+++}	Yes	No
Al^{+++}	No	-
Cd^{++}	No	-

Milian studied the oxidation of dulicitol and xylitol and found both reactions to be catalyzed by the ferric ion. He found that the

concentration of mannitol became constant after the reaction had proceeded for approximately twenty four hours. The mannitol-boric acid complex would not oxidize. Addition of the boric ion to a reaction solution containing ferric ion, mannitol and sodium hydroxide served to inhibit the reaction.

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12. Traube, Wilhelm and Kuhbier, Fritz, "Complex Ferric Compounds of Polyhydric Alcohols", Ber. 65B, 187-90 (1932).

13. Traube, Wilhem and Kuhbier, Fritz, "Autoxidation of Complex Iron Compounds of Polyhydric Alcohols," Ber. 65B, 190-195 (1932).

Notation

H_4E = erythritol

k_{35} = reaction velocity constant at $35^{\circ}C.$

k_{25} = reaction velocity constant at $25^{\circ}C.$

$\underline{M}$ = gram moles/liter

CHAPTER III

THEORY

The following sections are intended to give a background for the structures and reactions selected for the proposed mechanism. An important topic discussed in this chapter is the criteria for evaluation of the reaction regime, so that the results can be evaluated without interference from mass transfer effects.

A. Reaction Regime

Astarita,[1] lists five basic "regimes" of mass transfer with chemical reaction.

I. Kinetic regime - the reaction rate is so low that essentially all of the liquid phase is saturated with the gas.

II. Diffusional regime - the reaction rate is low enough not to interfere with the diffusive process, but yet is fast enough to consume the transferred component.

III. Fast reaction regime - the reaction is fast enough so that the reaction occurs in the boundary layer, keeping the concentration of the transferred component at its equilibrium value.

IV. Instantaneous reaction regime - the reaction is so fast that diffusion of other components to the reaction site may be limiting.

V. Surface reaction regime - the reaction proceeds essentially at the surface.

To study the reaction without interference of diffusional effects it is important to vary the reaction conditions so that the reaction may be studied in regime I. One of the assumptions is that the diffused component, in this case oxygen, participates in the rate controlling step or one that might become rate controlling. In this case also, the diffusional effects will not interfere with correlation of the data. The following criteria will be necessary for the existence of this regime.

1. An increase in temperature will result in a large change in reaction rate as predicted by the Arrhenius law. The increase in rate solely due to higher diffusion coefficients for a ten degree rise in temperature would be approximately 15%. For a reasonable activation energy, the increase due to the chemical reaction would be 50 - 150%.

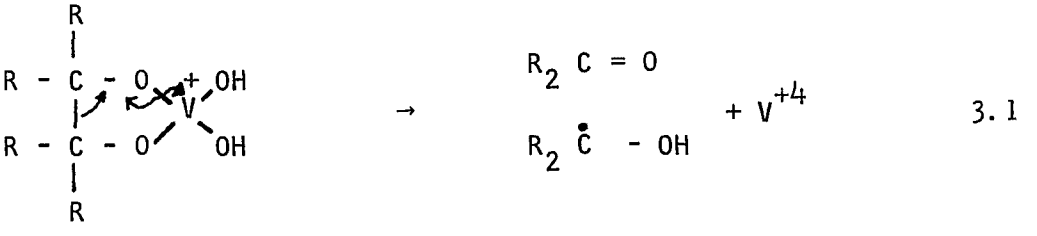
2. An increase in oxygen sparging rate will not affect the rate of the reaction. If the oxygen concentration affects the rate determining step, and the solution is unsaturated, the reaction rate would change upon an increased sparging rate, whereas for an oxygen saturated solution, increased sparging rate would have negilible effect.

3. Kinetics effects are obtained for variation in system parameters. Any change in reactant concentrations should result in rate changes, depending upon the particular system.

B. One Equivalent Versus Two Equivalent Oxidants

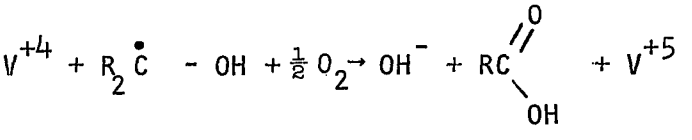
Ferric iron is considered to be a one equivalent oxidant. The highest oxidation state of iron is VI and is rare.[2] The only two readily accessible oxidation states are +2 and +3. The two electron oxidants act because of their ability to accept the transfer of two electrons to their outer shell, a feature that iron doesn't possess. With iron(III), the single electron is transferred to the available d orbital. Glycol cleavage by one electron and two electron oxidants is compared with the following mechanisms.[19]

One Electron Oxidant



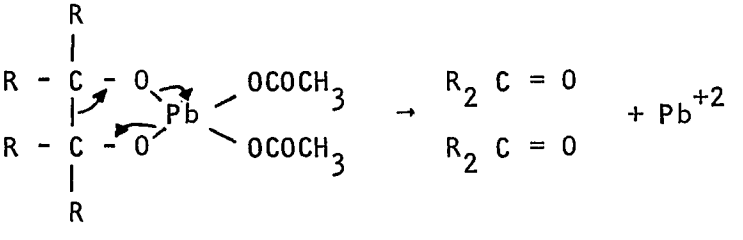
3.1

The radical $R_2\dot{C}-OH$ could then react with the reduced metal ion with the following result.



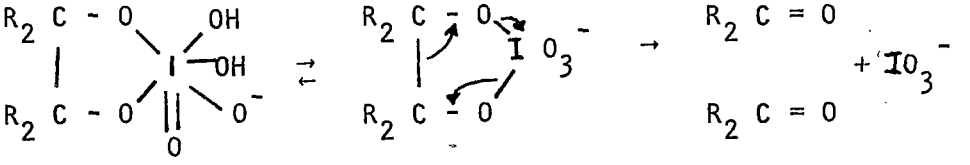
3.2

Two Electron Oxidant



3.3

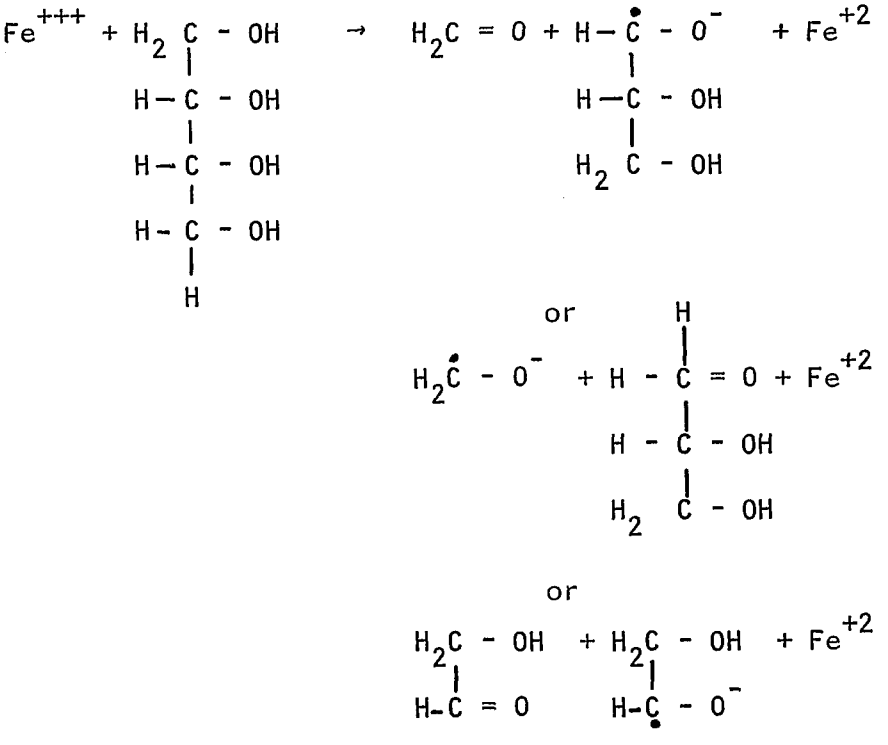
The periodic acid oxidation used in the analytical work (Chapter IV) also proceeds by a two electron mechanism.[20] The reaction is believed to proceed through a clyclic intermediate that decomposes as shown.[21]



3.4

(I^{+7}) (I^{+7}) (I^{+5})

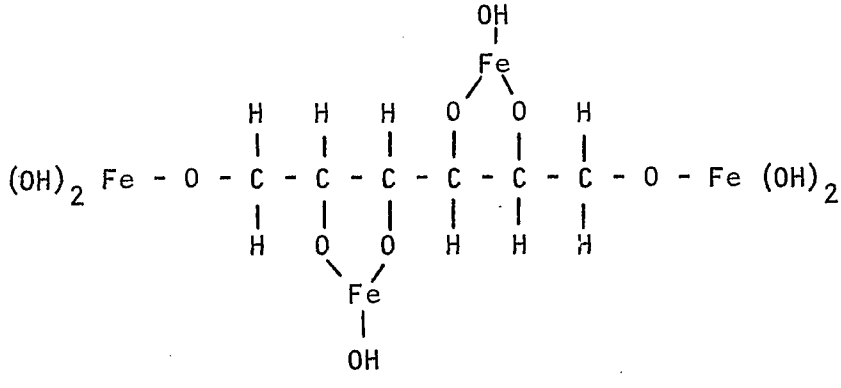
According to the above mechanism then, oxidation of erythritol by a one electron oxidant such as ferric ion might be expected to produce an aldehyde and a radical in the initial steps.



3.5

C. Possible Structure for Iron-Erythritol Complex

There is evidence for iron-erythritol and iron-mannitol[11] chelates, but determination of the structure has been made only by precipitation methods. Table (III-1) contains references for chelates with other ions. Structural determinations, by methods other than precipitation, of mannitol complexes with related metal ions do not agree with the results of the precipitation techniques. The precipitation method only determines the empirical formula of the compound precipitated. By the precipitation method the following structure is proposed for the iron(III)-mannitol complex in alkaline solution.



The formation of the chelate might occur in the following manner with the instability constants K_I, K_{II}, K_{III}, K_{IV}, (H_6 M = mannitol).

$$H_6M + Fe(OH)_3 \rightleftharpoons [H_4MFe(OH)] + 2H_2O \qquad K_I \qquad 3.6$$

$$[H_4MFe(OH)] + Fe(OH)_3 \rightleftharpoons [H_2MFe_2(OH)_2] + 2H_2O \qquad K_{II} \qquad 3.7$$

$$[H_2MFe_2(OH)_2] + Fe(OH)_3 \rightleftharpoons [HMFe_3(OH)_4] + H_2O \qquad K_{III} \qquad 3.8$$

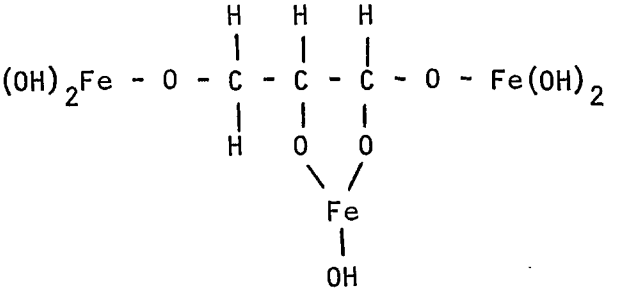
$$[HMFe_3(OH)_4] + Fe(OH)_3 \rightleftharpoons [MFe_4(OH)_6] + H_2O \qquad K_{IV} \qquad 3.9$$

Table (III-I)

Some References For Chelate Compounds of Erythritol and Mannitol.

Liquid	Central Ion	Reference
Erythritol	Molybdenum	13
Erythritol	Antimony	9
Erythritol	Iron(III)	17
Erythritol	Cu(II)	10
Mannitol	Molybdenum	13
Mannitol	Arsonic	14, 18
Mannitol	Boron	14, 18
Mannitol	Tellurium	6, 14
Mannitol	Antimony	9
Mannitol	Germanium	7
Mannitol	Iron(III)	17

For erythritol the corresponding complex would be;



The formation equation might be as follows, assuming that the precipitated compound has the same structure as the free compound in solution. (H_4E) = erythritol.

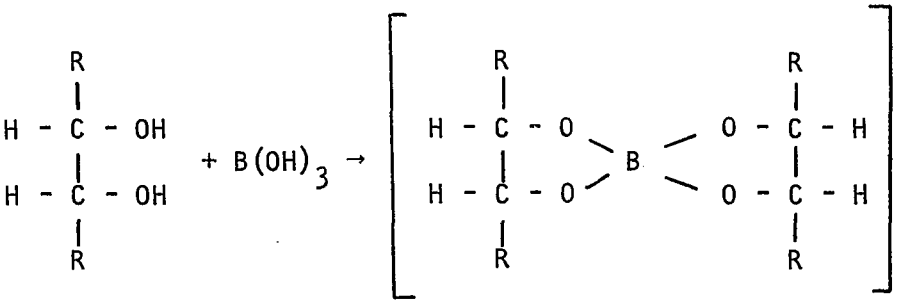
$$H_4E + Fe(OH)_3 \rightleftarrows [H_2\ EFe(OH)] + 2H_2O \qquad K_V \qquad 3.10$$

$$[H_2EFe(OH)] + Fe(OH)_3 \rightleftarrows [HEFe_2(OH)_3] + H_2O \qquad K_{VI} \qquad 3.11$$

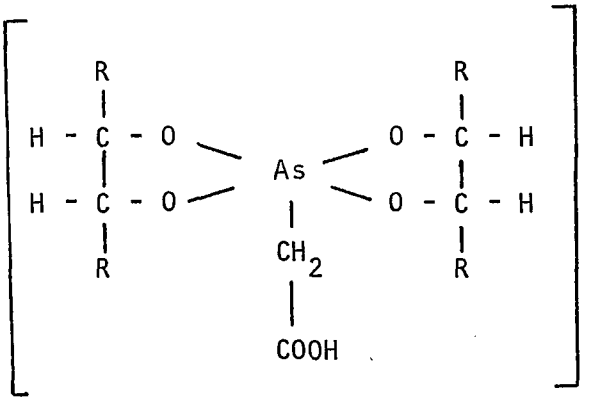
$$[HEFe_2(OH)_3] + Fe(OH)_3 \rightleftarrows [EFe_3(OH)_5] + H_2O \qquad K_{VII} \qquad 3.12$$

The Copper-Erythritol Complex[10] has also been characterized by a precipitation method and found to have the formula $C_4H_{10}O_6\ Cu_2$.

There is also evidence[3,7,8,9,14] for the formation of a complex between two or more polydentate ligand molecules and one central atom. Some examples of chelate compounds between 1,2-dihydroxy compounds and positive central atoms are as follows.



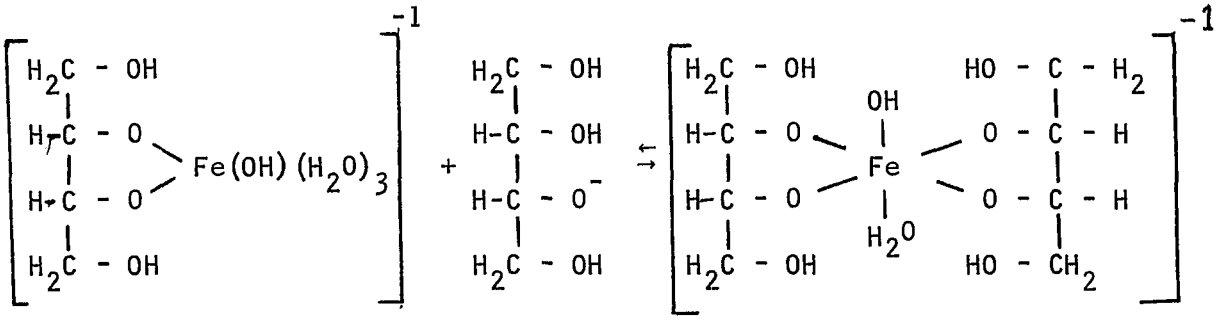
3.13



3.14

Everest and Harrison[7] have found evidence that germanium forms a 1:1 negatively charged germanium-mannitol complex up to a ph of about 8.0. Between a ph of 8.0 and 10.0 two complexes are formed, the 1:1 negatively charged complex, along with a 1:2 doubly charged di-mannitol complex. The 1:2 and a 1:3 complex[8] are formed above a ph of 10. The mannitol to germanate ion ratio was about 6 to 1. When a ratio of 1:1 was used the 1:1 complex was formed. Evidence was also presented for an uncharged mannitol-germanium complex when excess mannitol was present.

Erythritol should be sterically more favorable for a 1:2 or a 1:3 complex than mannitol. Since the ratio of erythritol to ferric ion in the present experiments are approximately the same as those used by Everest and Harrison, it is possible that the following equation may also be operative.



$$+ 2H_2O \qquad 3.15$$

D. Multi-Complex Mechanisms

There are several examples[4,5,6,15] in which the rate data could only be explained on the basis of more than one complex. In the manganesse catalyzed oxidation of oxalic acid by chlorine, Taube[20] has proposed the formation of two complexes between the manganese ion and oxalic acid to explain the rate data. The following equations constitute the proposed mechanism.

$$H_2C_2O_4 + Mn^{+++} \rightleftarrows MnC_2O_4^{+} + 2H^{+} \qquad 3.16$$

$$H_2C_2O_4 + MnC_2O_4 \rightleftarrows Mn(C_2O_2)_2^{-} + 2H^{+} \qquad 3.17$$

$$MnC_2O_4^{+} \xrightarrow[slow]{} Mn^{++} + C_2O_4^{-} \qquad 3.18$$

$$C_2O_4^{-} + Cl_2 \rightarrow CL + CL^{-} + 2CO_2 \qquad 3.19$$

$$CL + Mn^{++} \rightarrow Mn^{+++} + CL^{-} \qquad 3.20$$

Taube states that the rate of oxidation of the rate should be described by the following equation if, (1) the rate of decomposition is small,

(2) practically all manganic ion added is present as the mono-oxalate complex.

$$\frac{-\,d(CL_2)}{d\theta} = k_o[Mn(III)] \qquad 3.21$$

The k_o values calculated from the data increased with the oxalic acid concentration at low values, but not at high concentrations. The explanation of Taube is that as the oxalate concentration increases, the degree of complexing changes, favoring the non-reacting dioxalate complex. The experimental data was consistent with this explanation.

In later work by Taube,[15] he decided that in order to cover the entire concentration range three complexes are formed, $Mn\ C_2O_4^{+}$, $Mn\ (C_2O_4)_2^{-}$, $Mn\ (C_2O_4)^{\equiv}$ and each disproportionates at a different rate.

For the same system, Duke[5] stated that the rate of oxidation was merely the sum of the oxidation of the two complexes.

$$\frac{-d\,[Mn^{+3}]}{d\theta} = k_1[C_1] + k_2[C_2] \qquad 3.22$$

$[C_1]$ = concentration of $[Mn\ (C_2O_4)_2\ (H_2O)_2]^{-}$

$[C_2]$ = concentration of $[Mn\ (C_2O_4)\ (H_2O)_4]^{+}$

The following equation results from the mechanism.

$$\frac{-\,d\,[Mn^{+3}]}{d\theta} = \left[\frac{k_1K\,[H_2C_2O_4] + k_2\,[H^{+}]^2}{K\,[H_2C_2O_4] + [H^{+}]^2}\right][Mn^{+3}], \qquad 3.23$$

where K is the constant for the equilibrium between the two complexes.

Duke[4] also studied the cerate oxidation of 2,3 butanediol. He proposed the following mechanism.

I. Formation of cerate-butanediol Complexes

$$Ce\ (X)_6 + G \rightleftarrows Ce\ G(X)_4 + 2\ X \qquad 3.24$$

$$Ce\ (X)_4 + G \rightleftarrows Ce\ G_2(X)_2 + 2\ X \qquad 3.25$$

$$Ce\ G_2\ (X)_2 + G \rightleftarrows Ce\ G_3 + 2\ X \qquad 3.26$$

where G = 2,3-butanediol

X = OH^-, H_2O or any group coordinated with the cerate ion.

II. Disproportionation of Coordination Complexes

$$\frac{-\,d\,[Ce^4]}{d\theta} = k_1\,[Ce\ G\ (X)_4] + k_2\,[Ce\ G_2\ (X)_2] + k_3\,[Ce\ G_3] \qquad 3.27$$

The kinetics was expressed by the following equation.

$$\frac{-\,d\,[Ce^4]}{d\theta} = \frac{k_1K_1\,[G] + k_2K_1K_2\,[G]^2 + k_3K_1K_2K_3\,[G]^3}{1 + K_1\,[G] + K_1K_2\,[G]^2 + K_1K_2K_3\,[G]^3} \qquad 3.28$$

The kinetic data indicated that at low butanediol concentrations only the mono-diol complex reaction was significant, but at higher concentrations, the di and tri-diol complex reactions were appreciable.

E. Summary

Some of the conclusions that might be drawn from the investigations cited in Chapter II and III are as follows.

1. The theory of a multi-chelate complex with iron(III) and other transition metals is supported by other studies.
2. Ferric(III) ion is a one equivalent oxidant.
3. The autoxidation of mannitol does not occur by a long chain radical processes although the presence of hydroxyl radicals has not been ruled out.
4. The product of the oxidation of erythritol by ferrous ion and hydrogen peroxide is erythrose. Hydroxyl radicals are undoubtably present during this reaction.

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CHAPTER IV

APPARATUS AND PROCEDURE

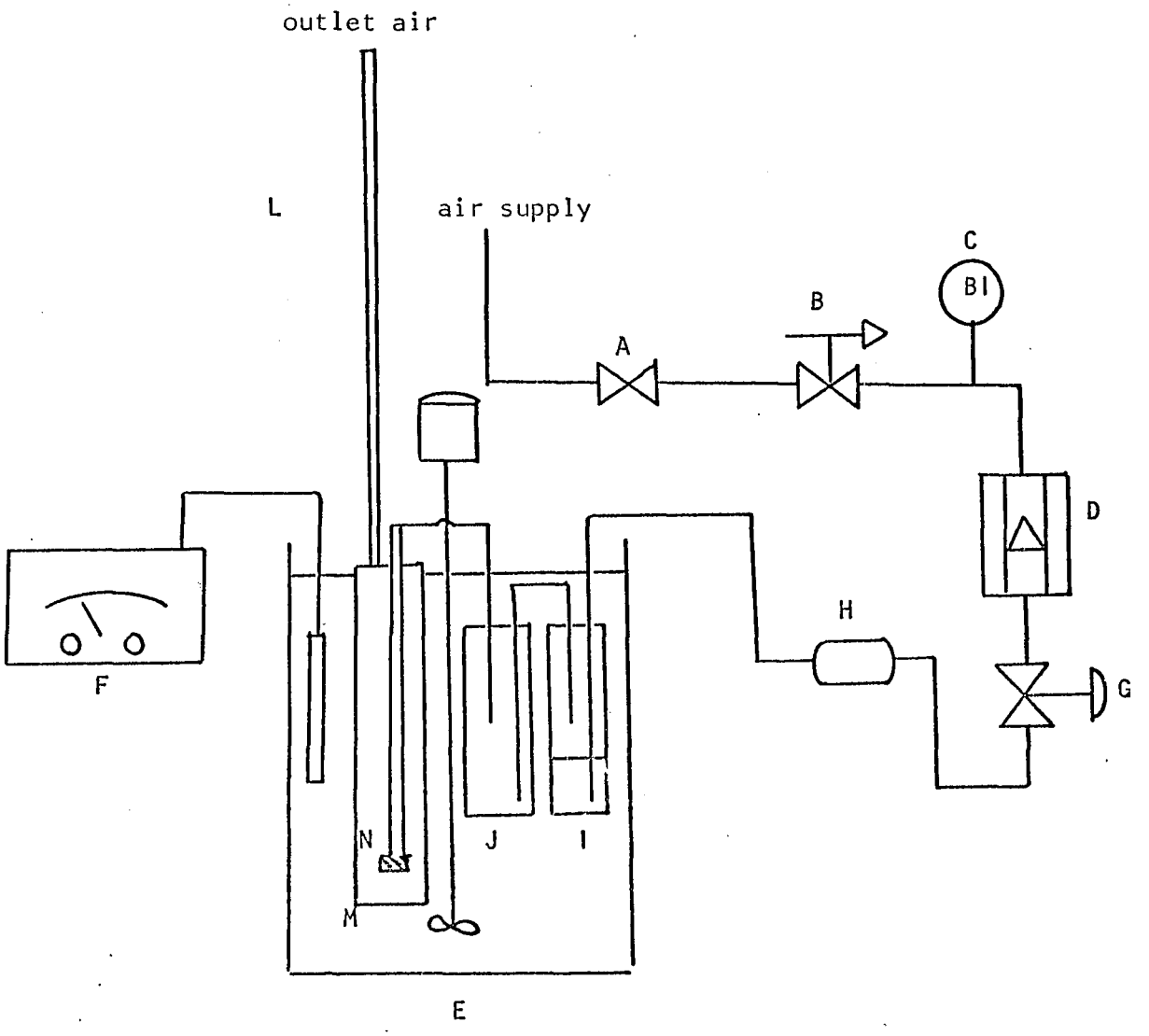
A. Introduction

The data are taken in a semi-batch gas sparged reactor. The initial alkaline solution of the erythritol-iron(III) complex is added to the 250 ml. glass reactor in which a fritted disk for sparging has been placed. After the sample equilibrates to the temperature of the bath, the gas sparging begins and small samples are taken at specified intervals. The method of analysis of the sample depends on whether the test has been made for rate data or for product distribution. The procedure for each analysis will be described in sections C and D.

B. Apparatus

1. Reactor

The reaction studies are conducted in a 1.7 inch diameter, 7.0 inch high gas sparged reactor. The effective liquid height used in the tests is about 5 inches. Figure (IV-1) is a schematic representation of the equipment employed. The temperature control of the water bath is achieved with a Model 1215A "Resistotrol" manufactured by Hallikainen Instruments of Berkeley California. The laboratory air is measured and controlled with a Brooks Instrument Company, Inc., Model 1355-1800 Sho-Rate "150" Rotameter with a self contained flow



Legend

A-gate valve	H-air scrubber-moisture and CO_2
B-pressure regulator	I-saturator
C-pressure indicator	J-intrainment separator
D-rotameter	K-agitator
E-constant temperature bath	L-entrainment tube
F-temperature controller	M-gas sparged reactor
G-control valve	N-fritted cylinder

Figure (IV-1)

Schematic diagram of reactor flow system.

controller. The float is constructed with monel and the metering tube from borosilicate glass. The selected accuracy of the meter is ± 3% of maximum scale from 100% to 10% of scale reading. A calibration curve for the meter is included in Appendix C.

Several transition periods are observed during the runs. The mass flow rate at which they occurred is dependent upon the porosity of the fritted gas dispersion tube used. The tube used is a Corning Glass gas dispersion tube with a 12 mm. O.D. extra coarse fritted cylinder. The nominal pore size is 170-220 microns. A pore size smaller than this is unusable because of excessive foaming. According to Braulick,[2] there are three bubble regimes for the air water system. Near spherical bubbles of 1/2" diameter are formed below a G_o of 8.5 lbs./hr.-ft.^{2}, from 8.5 to 25 lbs./hr.-ft.^{2} the bubble size increases, and above 25 lbs./hr.-ft.^{2} a sharp transition occurs in which bubble coalescence results in extreme turbulence. Braulick also mentioned the presence of "ionic" bubbles when the ionic strength of the solution is above .1 molar. The "ionic" bubbles are described as swarms of minute bubbles superimposed over the normal bubble dispersion pattern for pure water and air. The ionic bubbles are observed in the erythritol-iron(III) sodium hydroxide solution when the mass flow rate exceeded 10.0 lbs./hr.-ft.^{2}.

2. Gas chromatograph

The machine used for the analysis is a Micro-Tek GC-2500R. The GC-2500R is a dual column instrument with temperature programming capability and contains both a thermal conductivity and a hydrogen

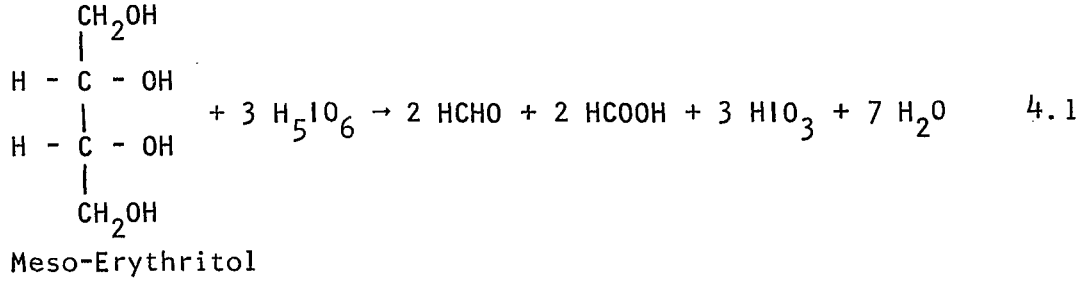
flame detection system. The carrier gas used was helium and the combustion gas hydrogen. Several columns were used for separation, but the most successful was a 6' x 1/8" column packed with neopentyl glycol succinate and SE-30. The calibration procedure is described in Appendix D.

C. Procedure for Kinetic Data

1. Erythritol

The periodic acid analysis[10,11] is used to obtain the erythritol concentration of the samples taken. Periodic acid reacts with carbon compounds containing adjacent hydroxyl groups. One mole of periodic acid is consumed for every adjacent hydroxyl group oxidized. Any unreacted periodic acid can be treated with potassium iodide to liberate the iodine, which is titrated with sodium thiosulfate. In the diol cleavage reaction, iodic acid is produced, which also liberates iodine when treated with potassium iodide. However, one mole of iodic acid liberates four moles of iodine whereas periodic acid liberates three. This difference in iodine liberated between a blank solution containing only periodic acid and the sample solution is a measure of the number of adjacent hydroxyl groups present. The following equations represent the reactions described above.

Glycol Cleavage



Meso-Erythritol

Iodine Liberation - Periodic Acid

$$2\ H_5IO_6 + 14\ KI + 7\ H_2SO_4 \rightarrow 7\ K_2SO_4 + 12\ H_2O + 8\ I_2 \qquad 4.2$$

Iodine Liberation - Iodic Acid

$$2\ HIO_3 + 10\ KI + 5\ H_2SO_4 \rightarrow 5\ K_2SO_4 + 6\ H_2O + 6\ I_2 \qquad 4.3$$

Some of the products formed that have adjacent hydroxyl groups, interfere by reacting with the periodic acid. The rate of reaction of the individual acid products vary also, so that even an analysis for total 1,2 diol content is inaccurate. Some of the typical rates of reaction with periodic acid are listed below.

Compound	Per Cent Reacted After 1.5 Hours	Per Cent Reacted After 17 Hours
Glycolic Acid	0.0	0.0
Erythritol	99.$^{+}$0	99.$^{+}$0
Glyceric Acid	72.0	85.0
Lactic Acid	5.0	24.5

In order to use the periodic acid for analysis of the erythritol, the reaction solution was treated with ion exchange resins to remove the acids. The reaction product could not be treated directly with the anion exchange resin because the negatively charged complex was

absorbed on the resins. The complex was first broken by removing the positive ferric ions with a cation exchange resin (Amberlite IR-120) and then the acids were removed with an anion exchange resin (Amberlite IRA-400). Several control tests were made to verify that the method would remove the acids. The details of the tests along with information concerning the ion exchange resins are included in Appendix B. The procedure used for the analysis is listed below. Sample calculations are given in Appendix B.

1. 10 ml. of the sample solution is pipetted into the top flask of the ion exchange train. The ion exchange apparatus contains the cation and anion exchange resins in series, packed in 10 mm. I.D. chromatographic tubes. (See Figure (B-1) for sketch of apparatus.)
2. The acid free sample and the column wash is then treated with 50 ml. of .1N periodic acid.
3. After 1 1/2 hours, an excess of potassium iodide crystals are added to the sample.
4. The liberated iodine is then treated with 10 ml. 6N sulfuric acid and titrated with standard sodium thiosulfate.
5. 10 ml. of distilled water is treated in identical fashion and the blank titrated with standard sodium thiosulfate.

2. Sodium hydroxide

The sodium hydroxide uptake was followed for each run. The samples were titrated to the phenolphthalein end point with standard

hydrochloric acid, immediately after being taken.

D. Procedure for Product Distribution

The lower weight hydroxy acid offer a difficult analysis problem when in dilute aqueous solutions. Several methods offered possibilities for quantitative analysis. "Wet" analytical methods[1,5] are available but the procedures are long and relatively large samples are required. Another possibility is the extraction of the acids from the aqueous solution into carbon disulfide using a liquid phase ion exchange resin, amberlite LA-2. Dolinsky and Wilson[3] were able to solubilize oxalic and glyceric acid by use of this liquid ion exchange resin. The resulting solution is then analyzed by infrared spectrophotometery. For this method also, the sample size must be relatively large.

The method that seemed to offer the most advantages was the formation of derivatives that could be analyzed by gas chromatography. The methyl esters are volatile and can be formed by reaction with diazomethane.[4,7] Another method, that previously has not been applied to the lower molecular weight acids, is the formation of the trimethyl silyl ethers of the acids and subsequent gas chromatographic analysis.

The analysis for erythritol by formation of the trimethyl silyl ethers has been demonstrated.[8,9] The latter method was selected because the erythritol concentration could be determined along with the acid concentrations, with little extra effort.

1. Gas chromatographic analysis

Ten millimeter samples are freed from cations by a column containing amberlite IR-120 cation exchange resins. The column is

identical to the cation exchange column described in Appendix B. The columns are washed with 60 milliliters of distilled water and a portion (usually 1/6th) of the solution evaporated to dryness in a vacuum oven at 40°C.

The evaporated samples are then treated with the reagent solution to form the derivatives. The reagent used is "Tri-Sil", a formulation sold by Pierce Chemical Company. "Tri-Sil" contains pyridine as a solvent, plus hexamethyldisilazane and trimethylchlorosilane. The samples are then heated for 4 minutes at 60°C and the precipitate allowed to settle. The clear liquid is injected into the gas chromatograph.

The compounds related to the lower molecular weight acids that are characterized by the silyation procedure are shown in Figures (I V-II) and (I V-III). The calibration curves for the compounds are presented in Appendix D.

The peaks for the lactic and glycolic acid derivatives could not be resolved on the Se-30 column. Several types of packing were tried in columns of various lengths and diameters. The hydrogen flame detector was used to obtain greater sensitivity. The peaks were finally resolved on a 6' x 1/8" stainless steel column packed with 1% neopentyl glycol succinate and 2% Se-30 on J.M.H.P. chromsorb B 100/120.

The major components of the reaction products were glycolic acid, glyceric acid, erythritol, formic acid, and carbon dioxide. The calibration curves for glycolic acid, glyceric acid and erythritol are included in Appendix D. In Figure (I V-IV) a typical output trace of the product solution is given.

Thermal conductivity detector, S.S. 2' x 1/4" column packed with 5% SE-30.

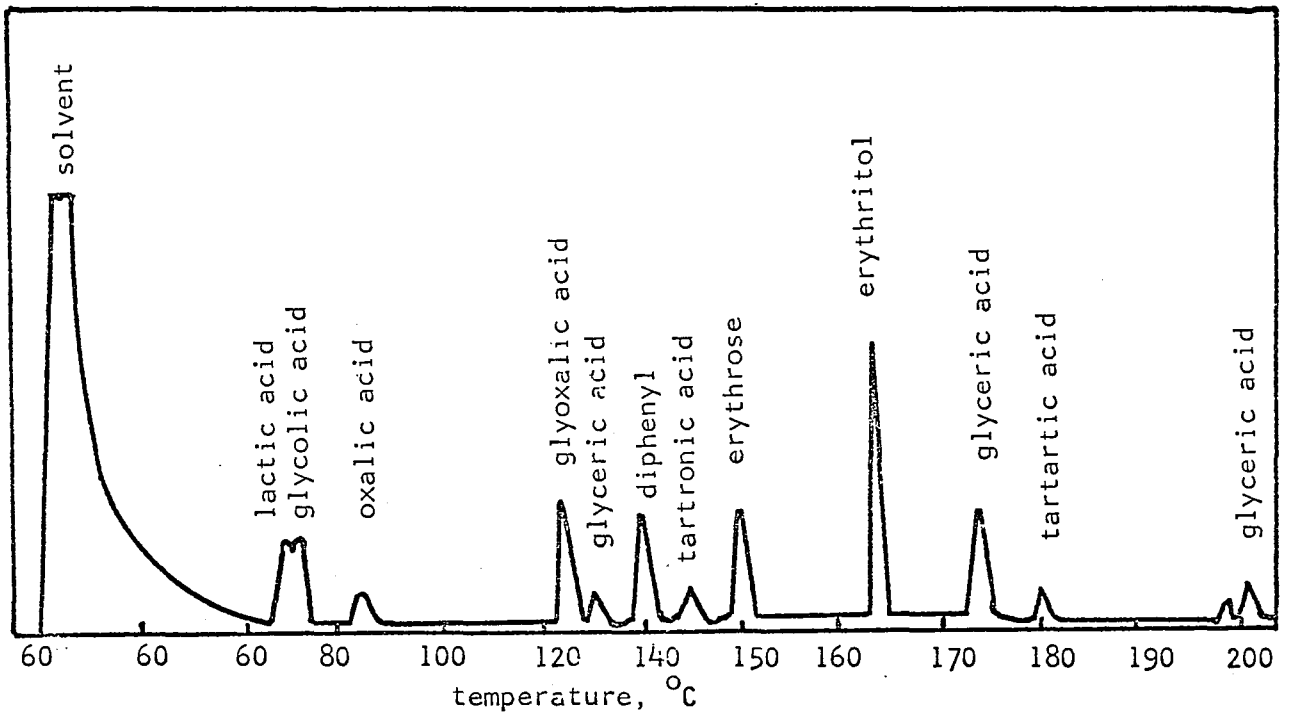


Figure (IV-11)

Output trace of trimethylsilyl derivatives of related hydroxy compounds.

Hydrogen flame detector, S.S. 6' x 1/8" column packed with 1% neopentyl glycol succinate and 2% SE-30.

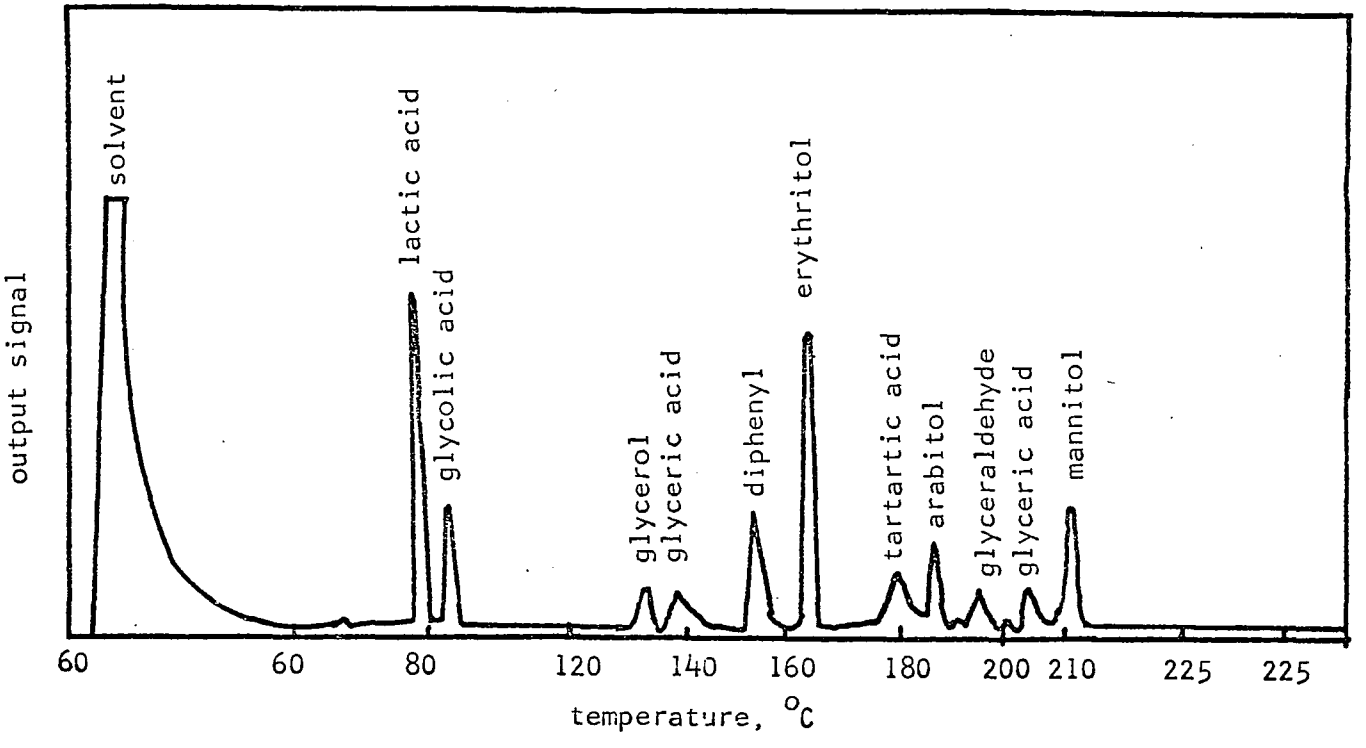


Figure (IV-III)

Output trace of trimethylsilyl derivatives of related hydroxy compounds.

Hydrogen flame detector, S.S. 6' x 1/8" column packed with 1% neopentyl glycol succinate and 2% SE-30.

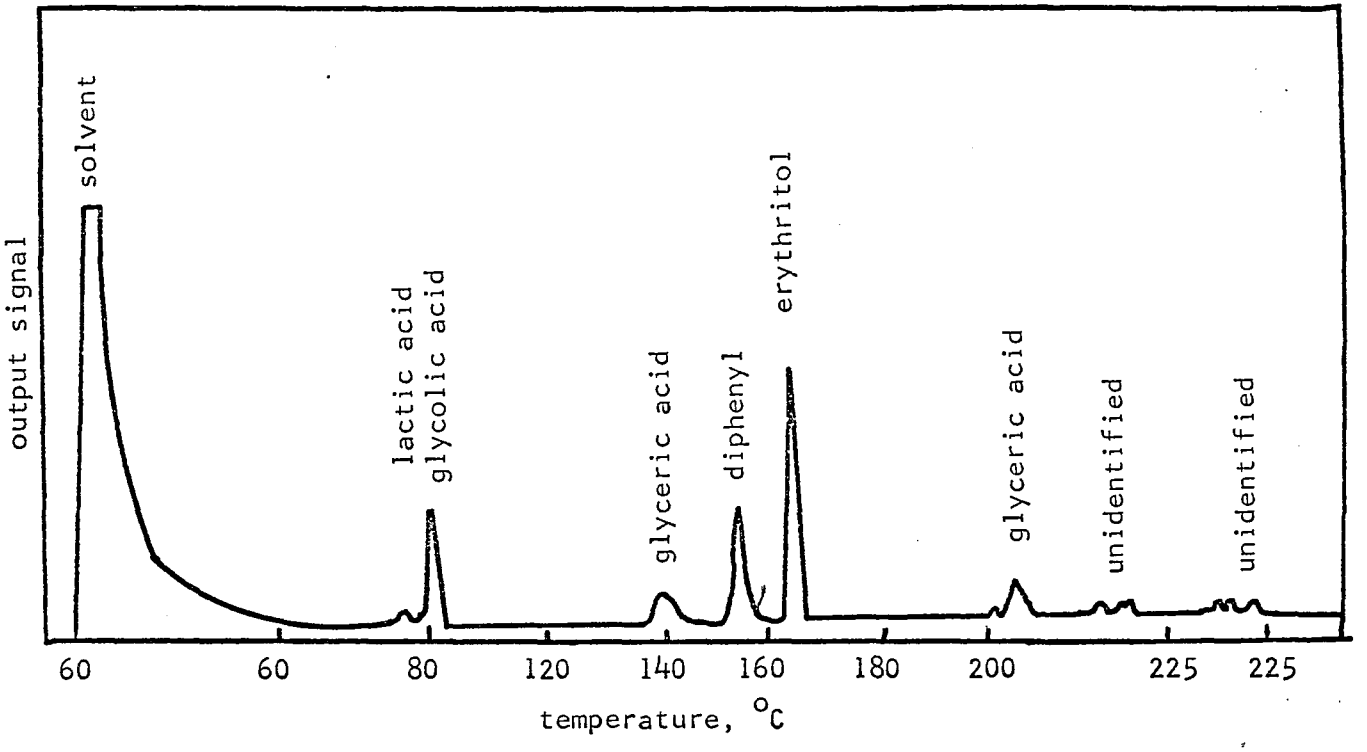
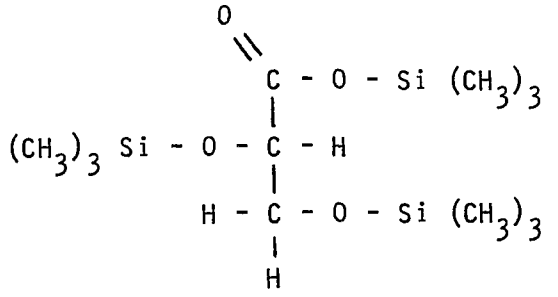


Figure (IV-IV)

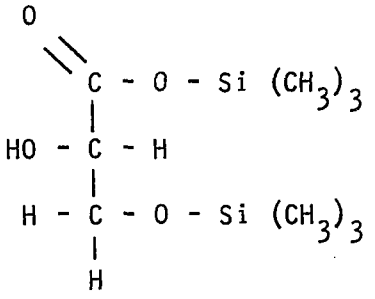
Output trace of trimethysilyl derivatives of reaction products.

A standard procedure was finally adopted for the analysis. The exact conditions are included in Appendix D and are only summarized here. The sample of approximately .5μL was injected into the vaporizer and the column temperature was held at 60°C for three minutes. The temperature programmer then began heating the column at a rate of 14°C/min. When the column temperature reached 225°C the temperature was held constant for four minutes, and then returned to 60°C for the next analysis.

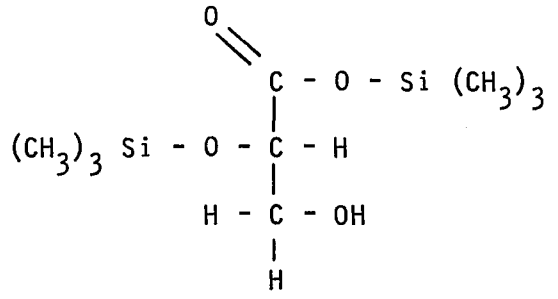
As shown in Figure (IV -III), glyceric acid gives three major peaks. The three peaks are probably due to the following three derivatives



I



II



III

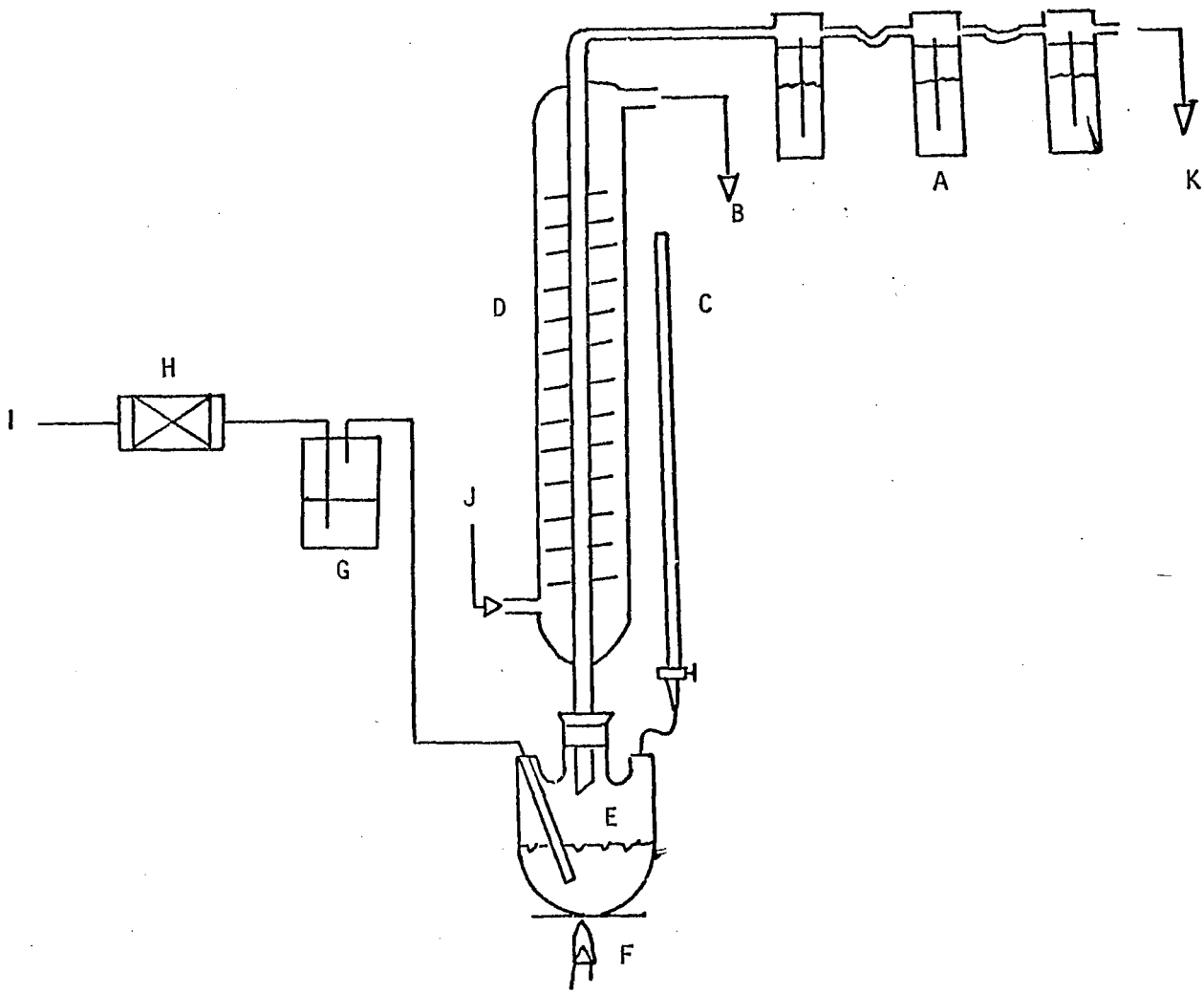
The peak at 88°C is probably I and the peaks at 200 and 201 II and III. The peak at 88°C was calibrated with the calcium salt of glyceric acid and the peaks at 200 and 201 were calibrated with glyceraldehyde. The calibration curve and results of a control test are included in Appendix D.

2. Carbon dioxide analysis

The carbon dioxide is measured by acidification of the sample, heating, and absorption of the liberated carbon dioxide in barium hydroxide. The carbon dioxide is stripped from the acid solution by means of air that had been dryed and freed from carbon dioxide. The barium carbonate is filtered in porous abundum crucibles and dryed in an oven until a constant weight is obtained. Sample calculations are given in Appendix B.

3. Formic acid analysis

After the carbon dioxide has been purged, the formic acid is determined by the method of Reid and Weihe.[6] The solution is treated with mercuric acetate and the carbonic acid stripped from the solution and absorbed in barium hydroxide as before. Figure (IV -V) is a schematic representation of the apparatus. The test is considered nearly specific for formic acid, as glycerol, oxalic acid, lactic acid, acetaldehyde and other related compounds[6] will not interfere with the tests. Glyceric acid was tested and does not react with mercuric acetate. The experimental procedure is outlined in Appendix B.



A-gas washing bottles - filled with barium hydroxide

B-cooling water outlet

C-measuring buret for addition of mercuric acetate and HCl

D-condenser

E-reaction flask

F-heat source

G-air purification-CO_2 removal, $BA(OH)_2$

H-air purification-ascarite

I-air inlet

J-cooling water inlet

K-vacuum

Figure (IV-V)

Schematic diagram of apparatus used for determination of formic acid and carbon dioxide.

E. Spot Tests

Several spot tests were made of various product solutions for specific compounds. Details of the tests used are included in Appendix D.

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Notation

G_o = Mass velocity of air (superficial) lbs./hr.-ft.^{2}

Se-30 = A silicon oil, liquid phase column packing, general purpose

μL = Microliter, 10^{-6} liters

CHAPTER V

EXPERIMENTAL DATA

A. Introduction

Ethylene glycol and glycerol were tested to see if they would complex and oxidize. Ethylene glycol did not form a complex, as evidenced by the precipitation of ferric hydroxide from the alkaline solution. Glycerol readily formed a complex but would not oxidize. (See Figure (V-I).)

Erythritol was tested and found to complex easily and to be susceptible to air oxidation. Tests were made to see if oxygen and a catalyst are both necessary to sustain oxidation. There is no measurable rate of oxidation, as shown in Figures (V-II) and (V-III), in the absence of either component. The alkali "uptake" is also a measure of the oxidation rate, and was negilible for the three tests. The kinetic data for the effect of each variable are presented in the following sections.

B. Temperature

Tests were made at temperatures ranging from $30^{o}C$ to $45^{o}C$. The solution at $45^{o}C$ was dark throughout the test. The results are shown in Figures (V-IV) and (V-V). A collodial precipitate was formed in the solutions at $40^{o}C$ and $45^{o}C$ as erythritol concentration was reduced to approximately the concentration of the ferric ion.

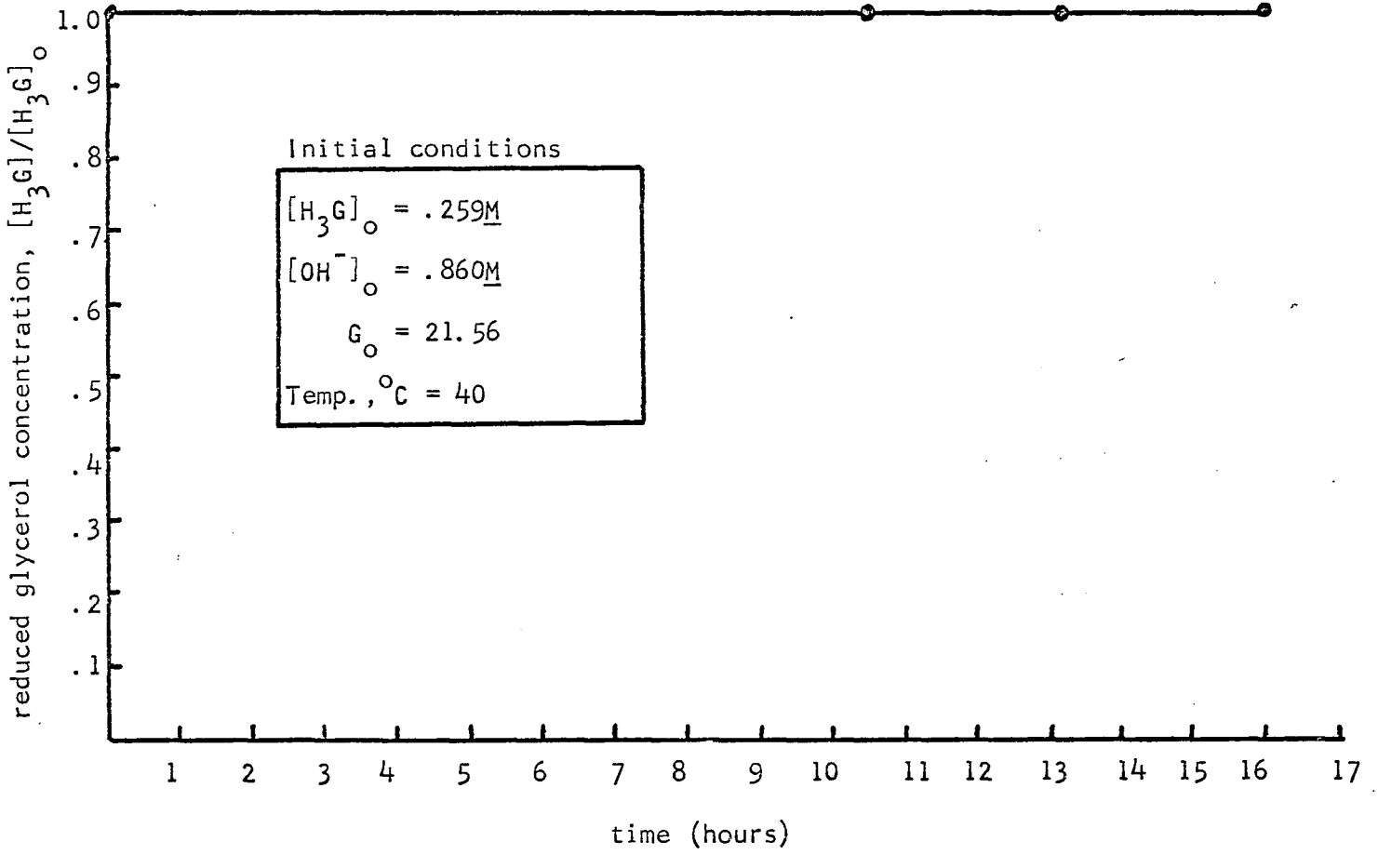


Figure (V-1)

The oxidation of glycerol.

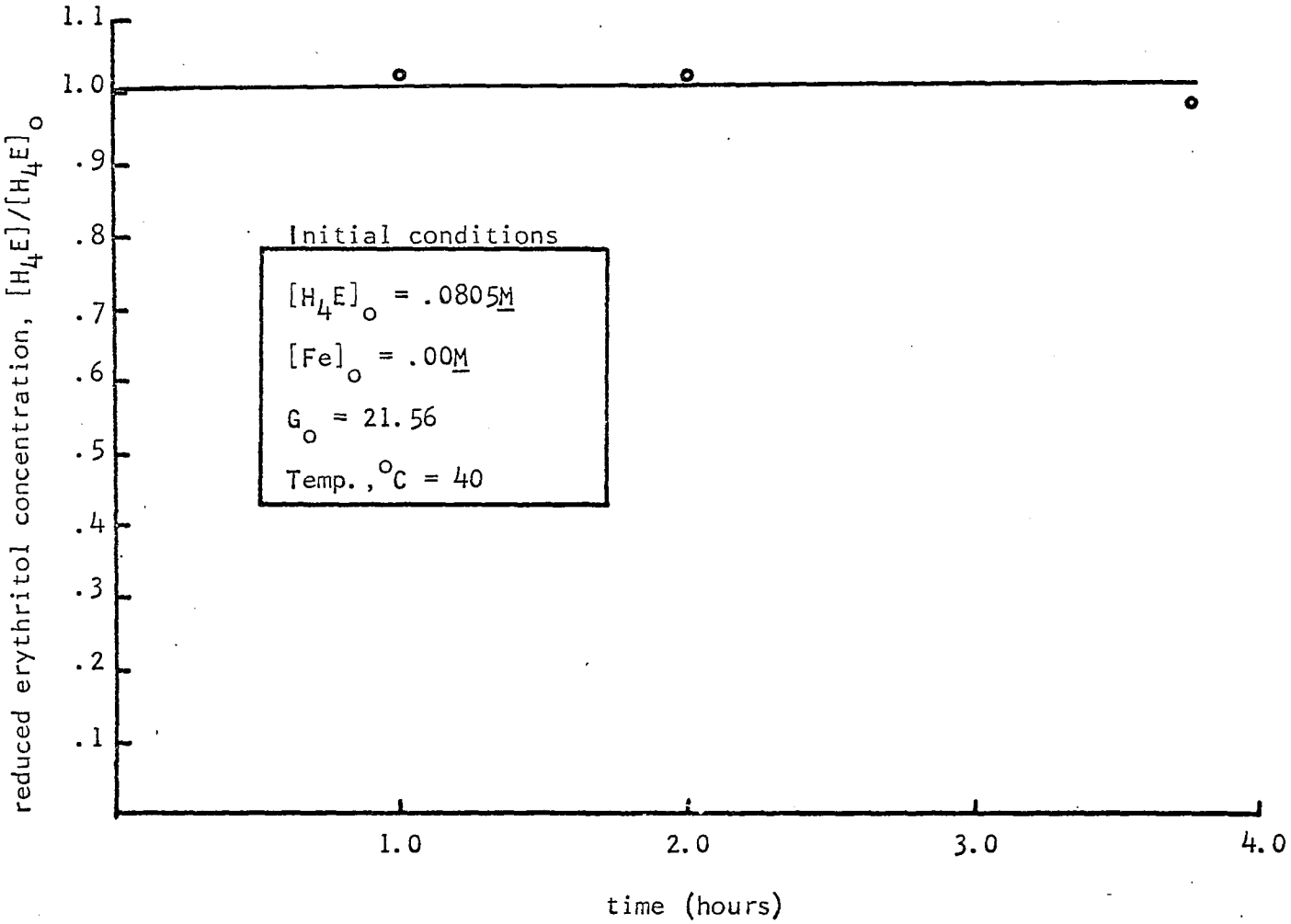


Figure (V-11)

Oxidation of erythritol in the absence of catalyst.

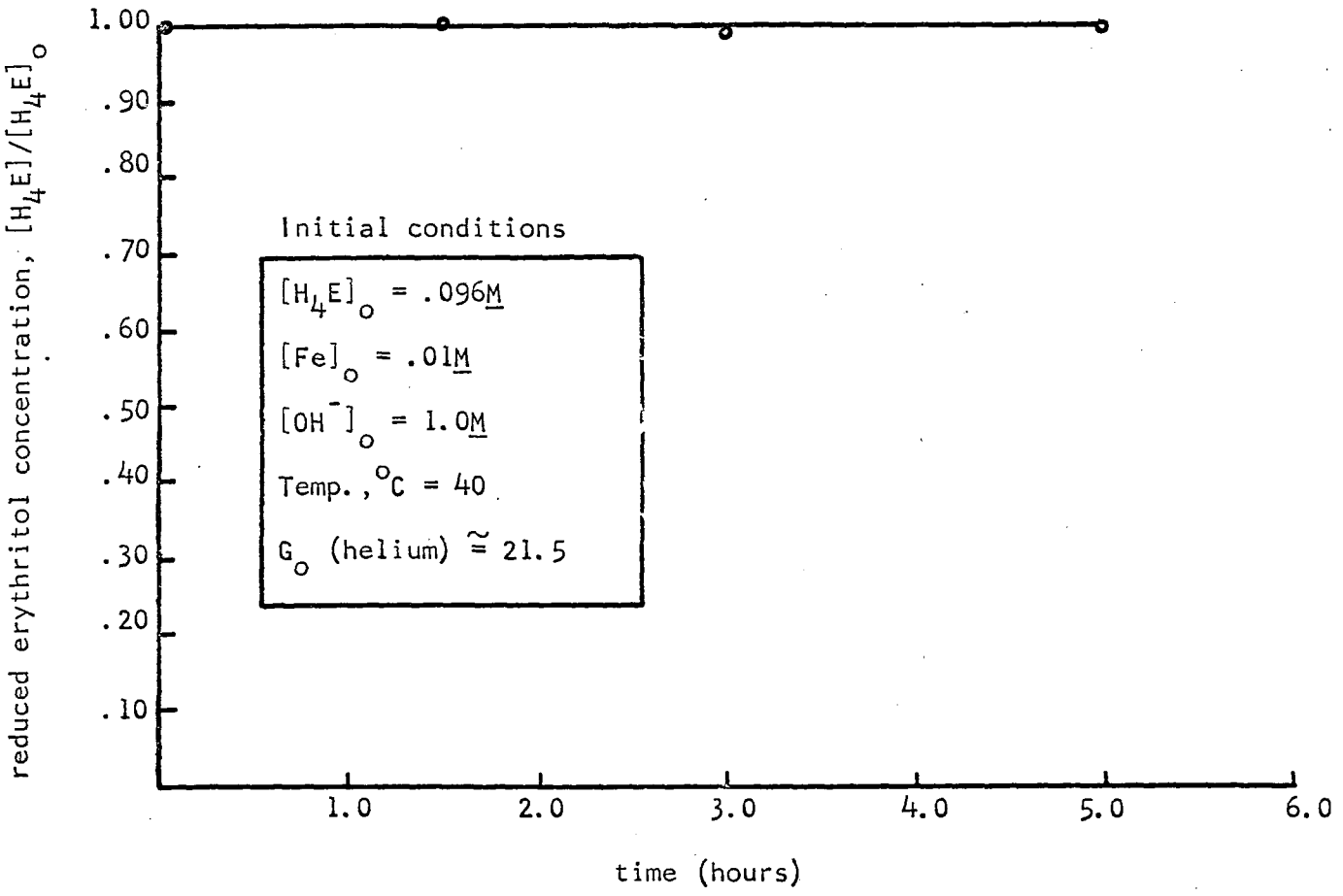


Figure (V-III)

"Oxidation" of erythritol with an inert gas.

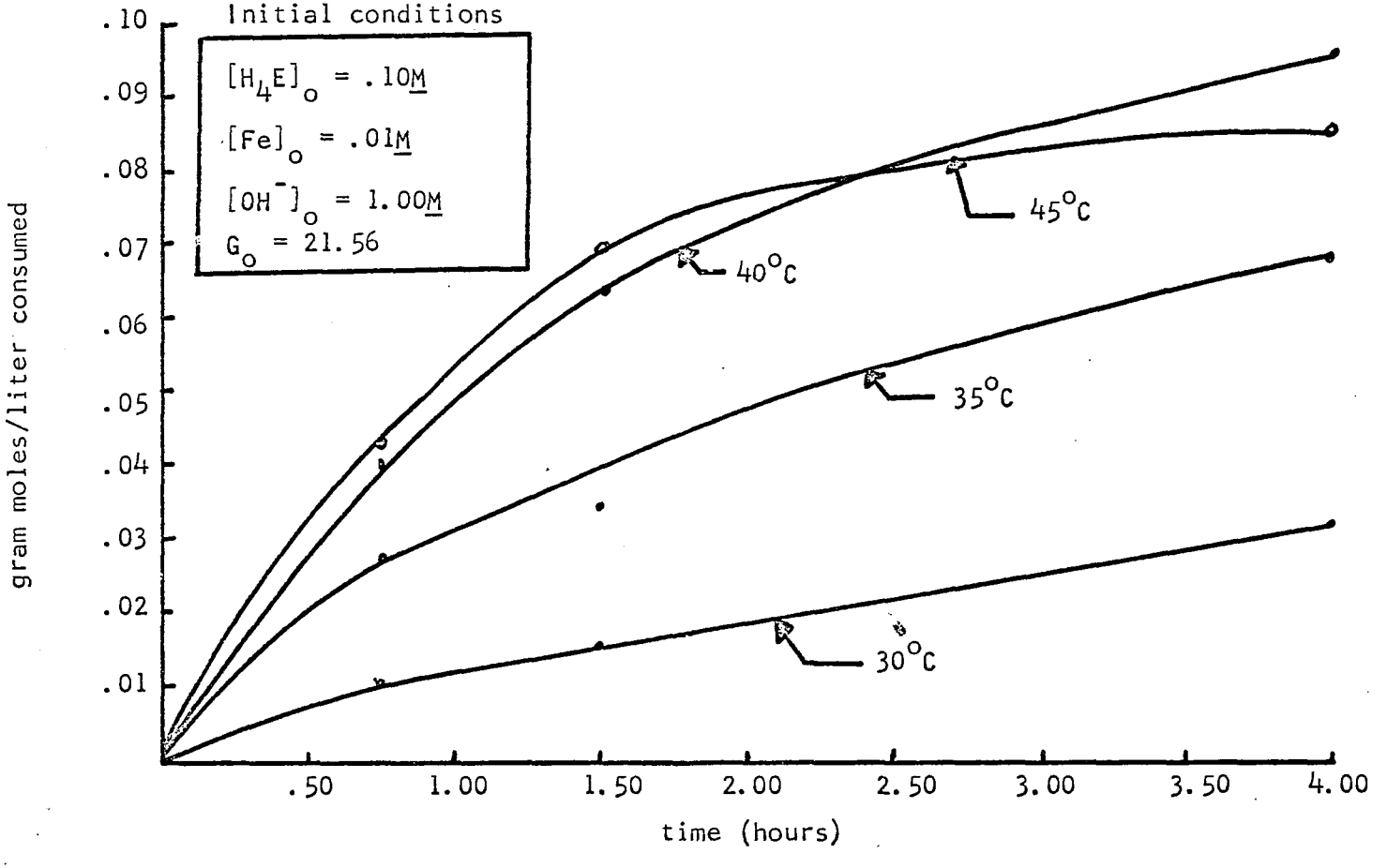


Figure (V-IV)

The effect of temperature - erythritol consumed.

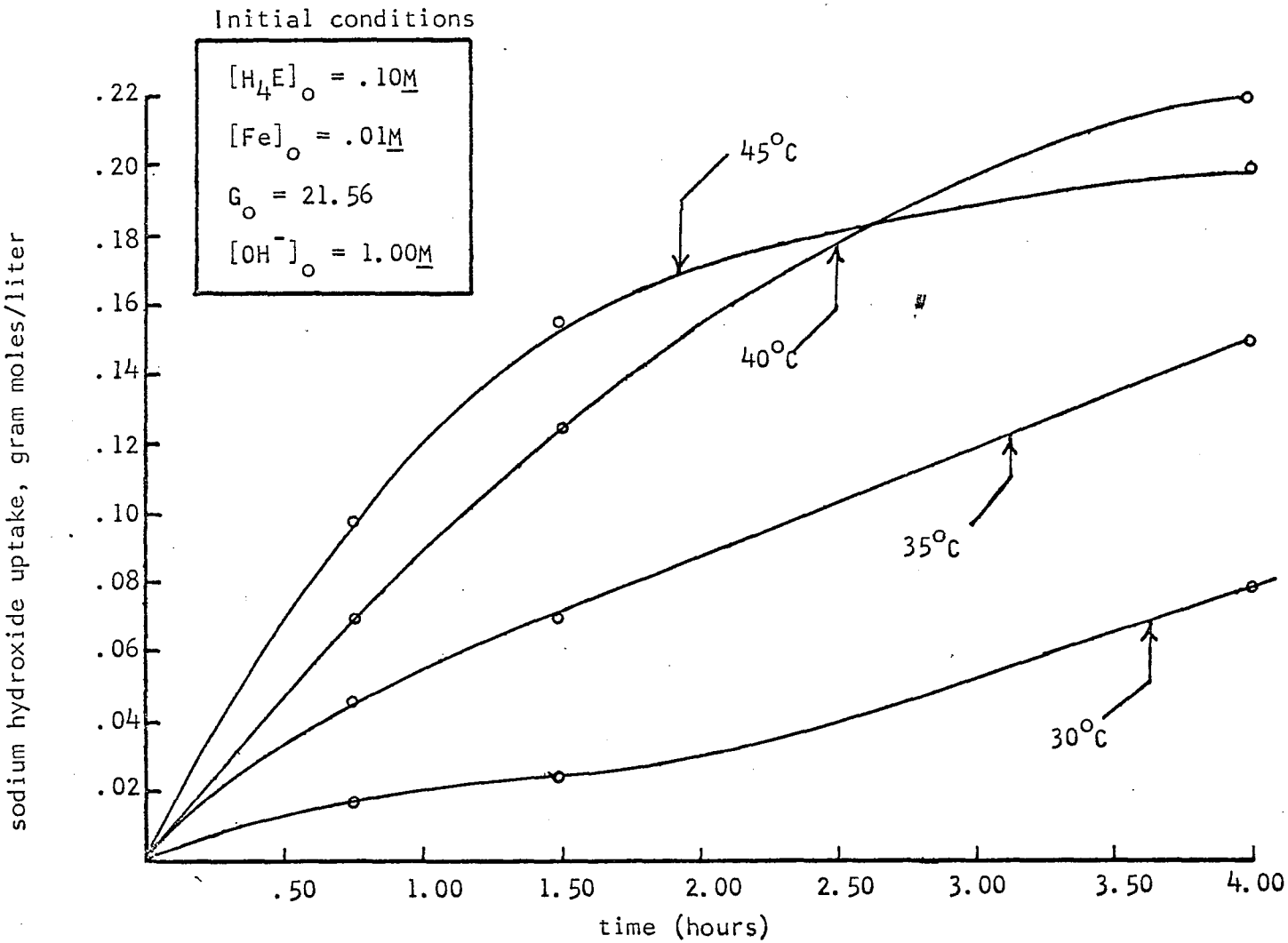


Figure (V-V)

The effect of temperature-sodium hydroxide uptake

C. Air Flow Rate

To prevent liquid entrainment and foaming, the highest practical mass flow rate is approximately 35 lbs./hr.-ft^2. Several tests were made with varying mass flow rates at 35^{o}C. The results are shown in Figures (V-VI) and (V-VII).

D. Initial Catalyst Concentration

The initial conditions were held constant except for the ferric chloride concentration. A catalyst concentration above about .04M for a .10M erythritol solution could not be studied as the erythritol could not prevent precipitation of ferric hydroxide. The results of the tests are presented in Figures (V-VIII) and (V-IX).

E. Erythritol Concentration

Several tests were made at varying initial erythritol concentration with the ferric chloride concentration, temperature, air flow rate and sodium hydroxide concentration, .01M, 35^{o}C, 21.56 lbs./hr.-ft.^{2} and 1.0M respectively. Run E-24, in which the initial erythritol concentration was .048M, was dark brown and became turbid after about two hours. All other solutions were clear yellow. The concentration range was .048M to .30M. Results of the tests are presented in Figures (V-X) and (V-XI).

F. Effect of Ph

A series of tests were made to study the effect of hydroxide ion concentration on the rate of the reaction. The results are shown in Figures (V-XII) and (V-XIII).

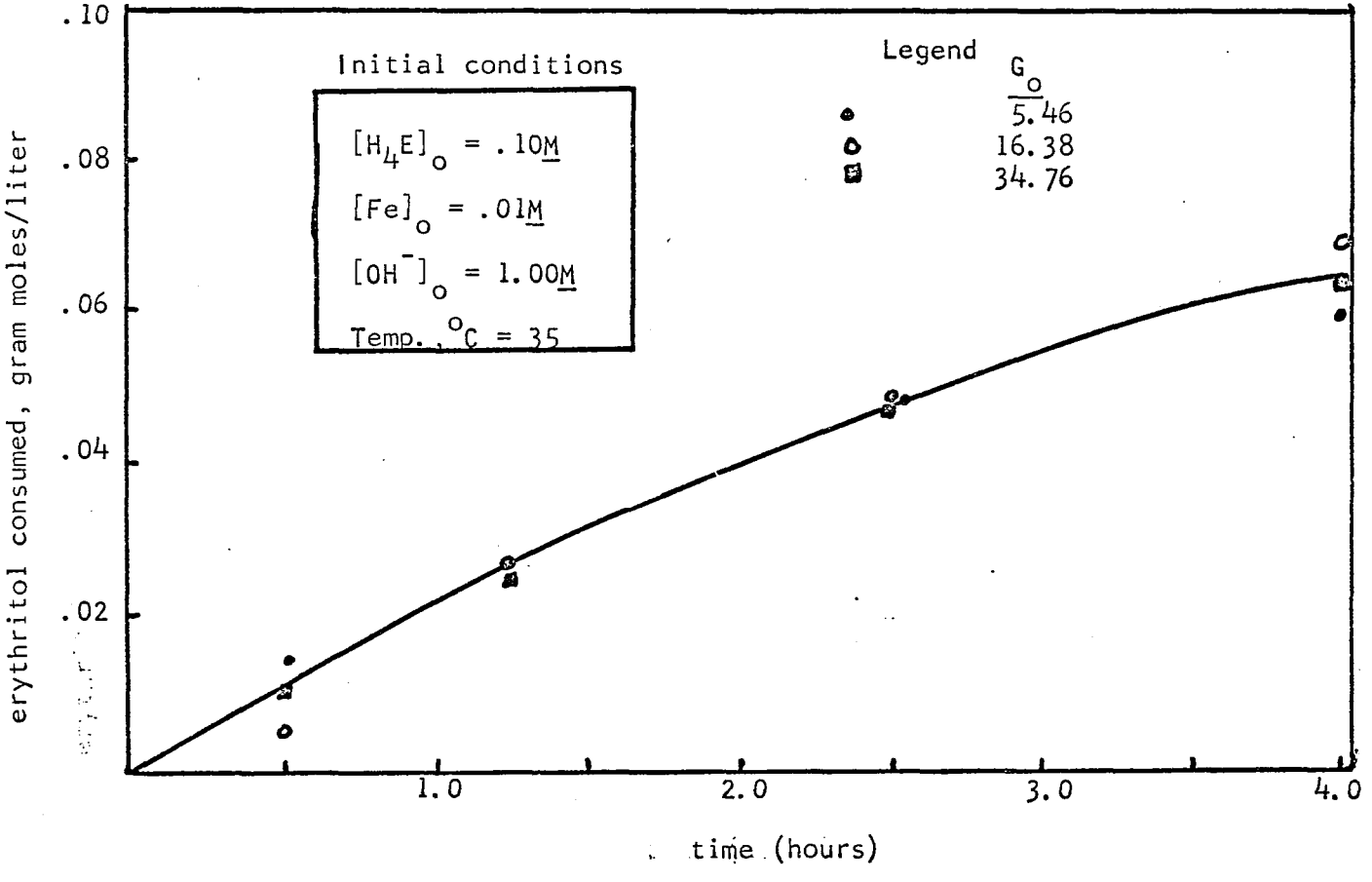


Figure (V-VI)

The effect of air rate - erythritol consumed.

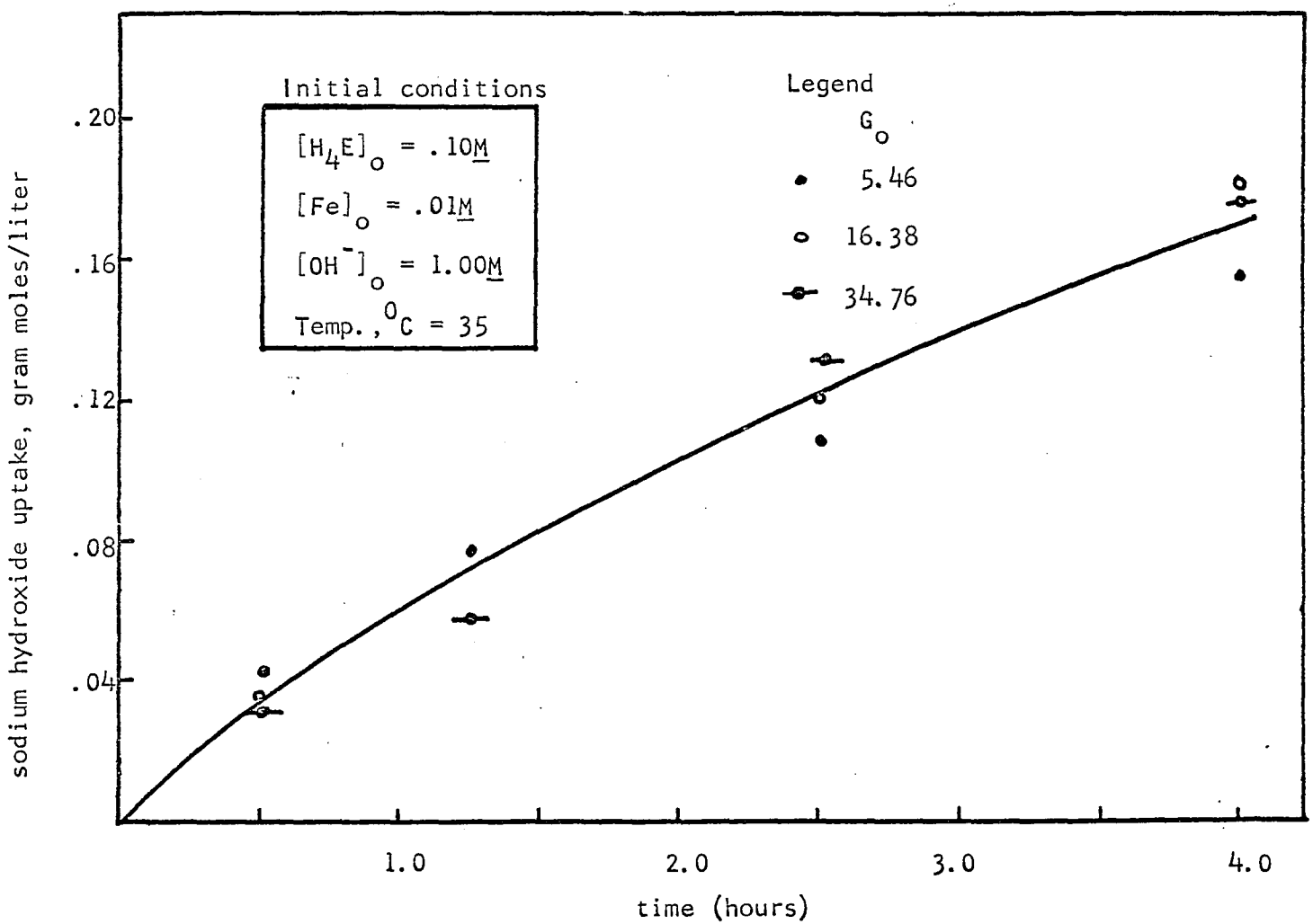


Figure (V-VII)

The effect of air rate - sodium hydroxide uptake.

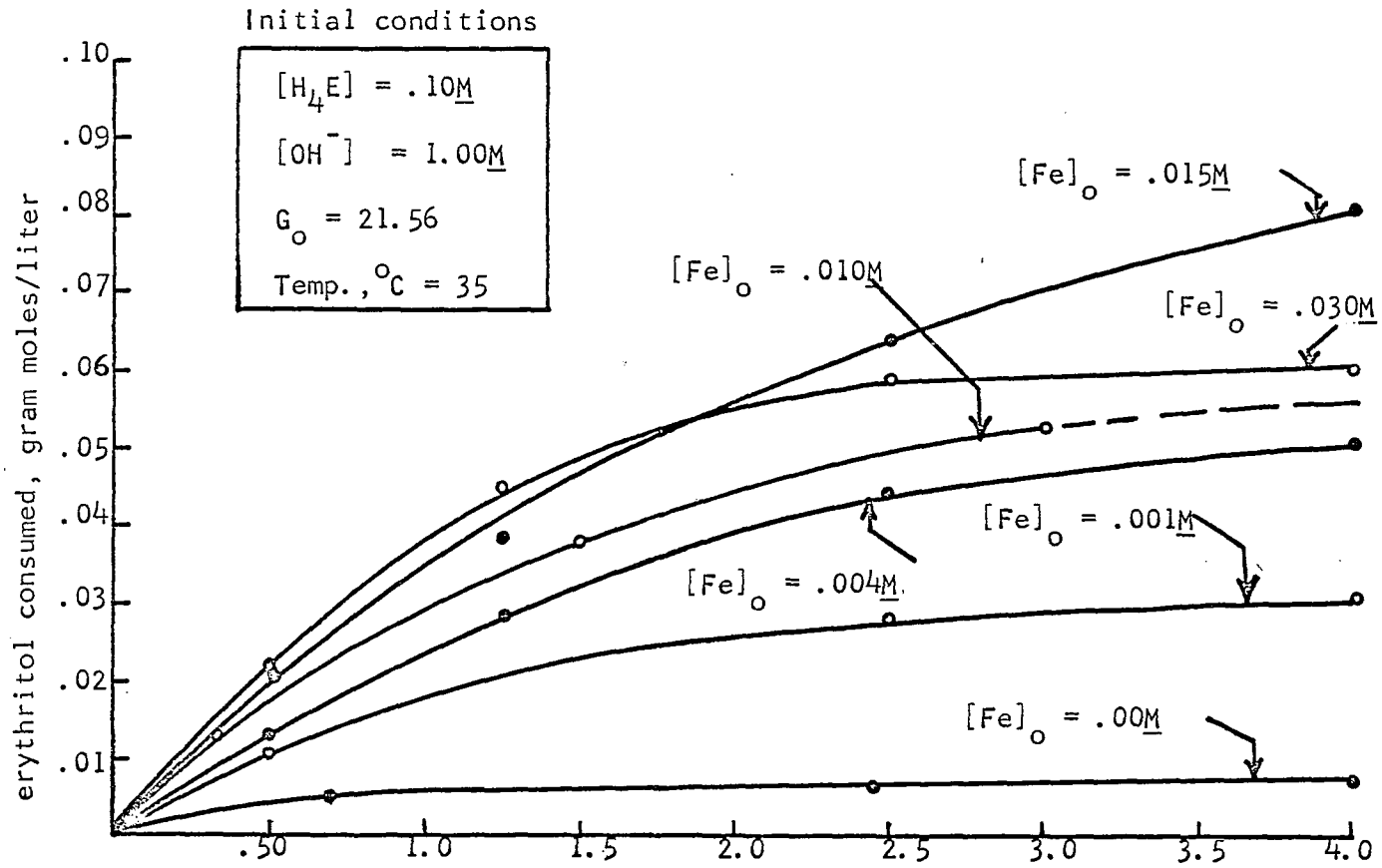


Figure (V-VIII)

The effect of catalyst concentration-erythritol consumed.

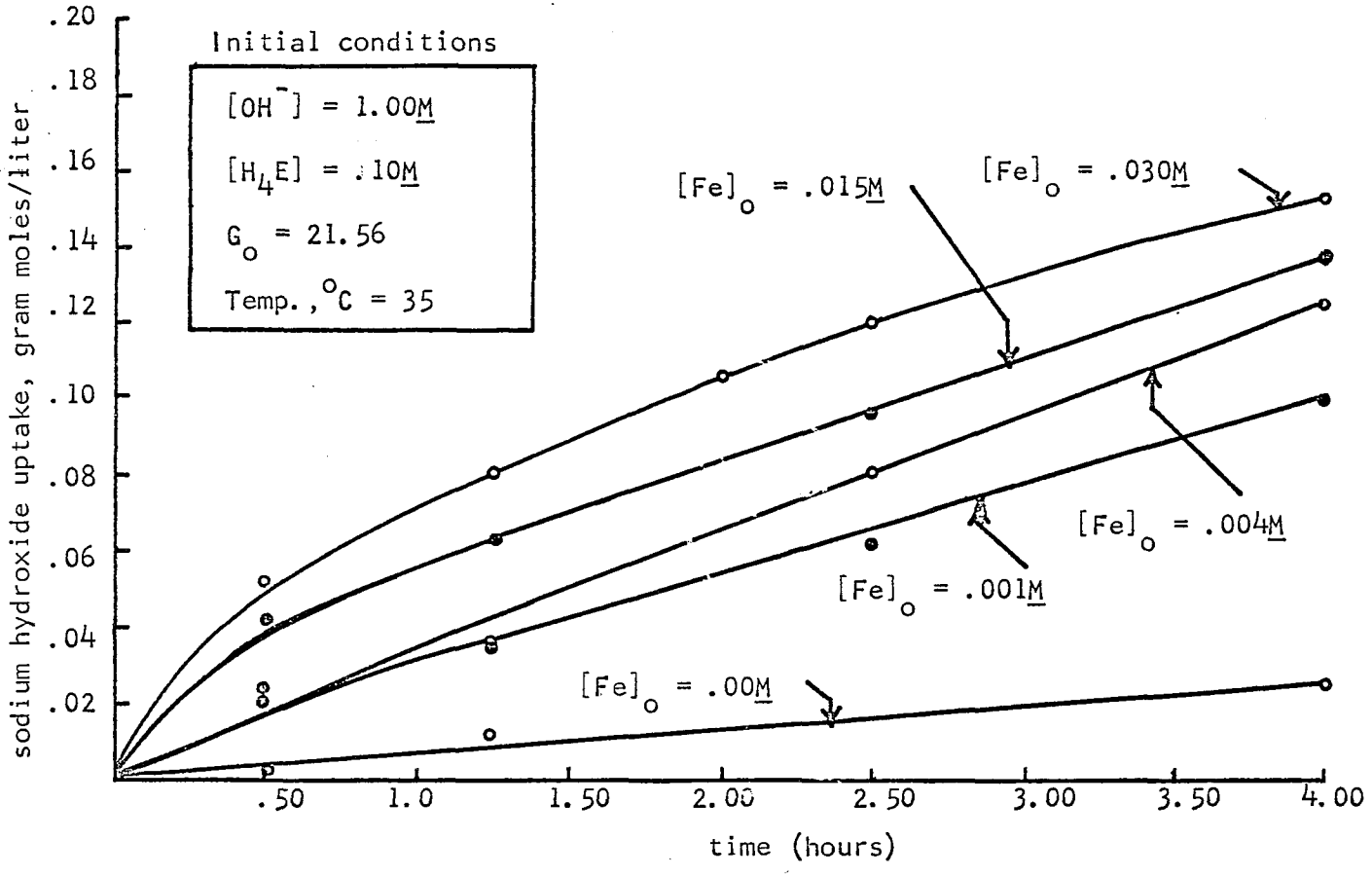


Figure (V-IX)

The effect of catalyst concentration-sodium hydroxide uptake.

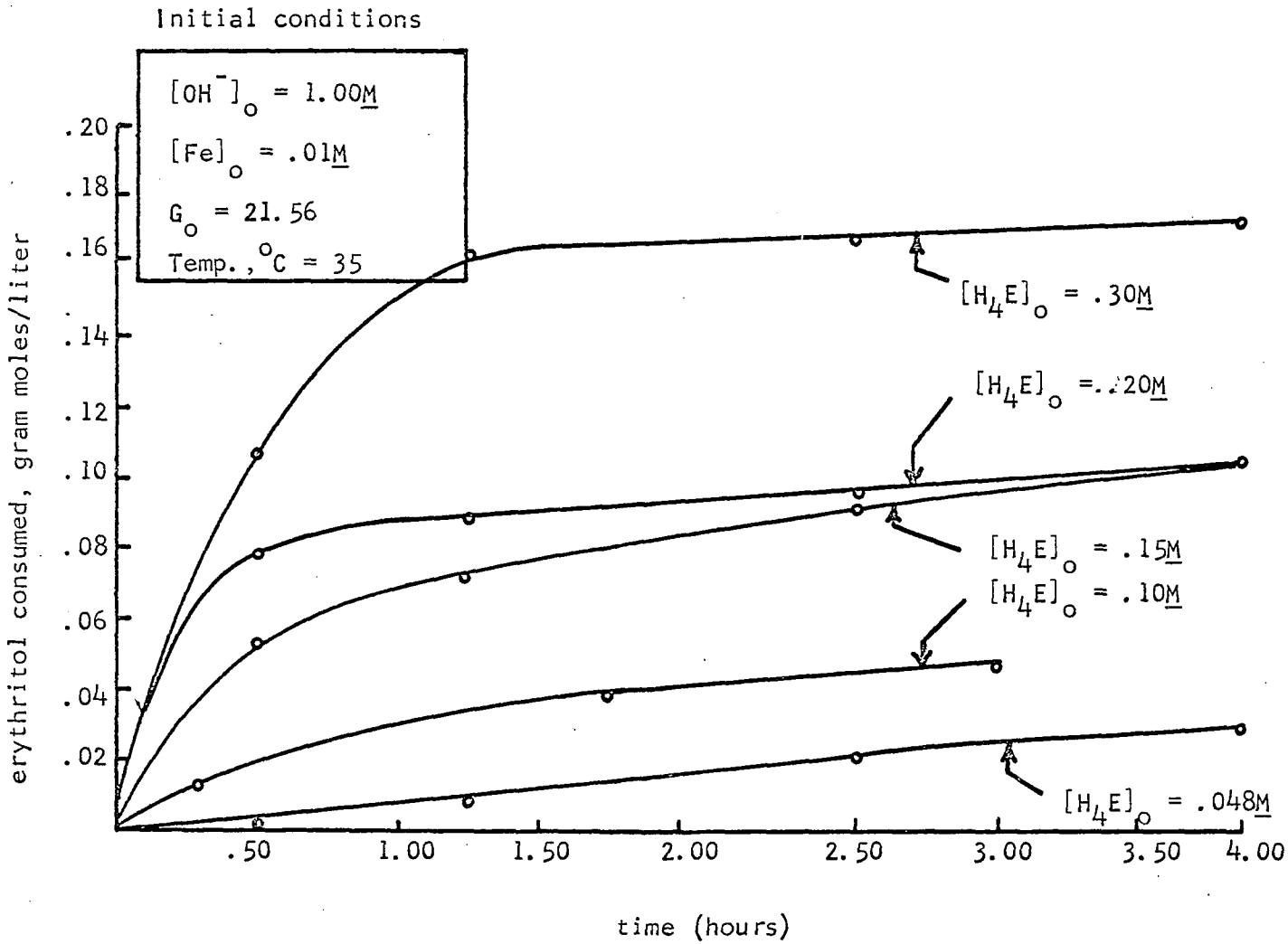


Figure (V-X)

The effect of initial erythritol concentration-erythritol consumed.

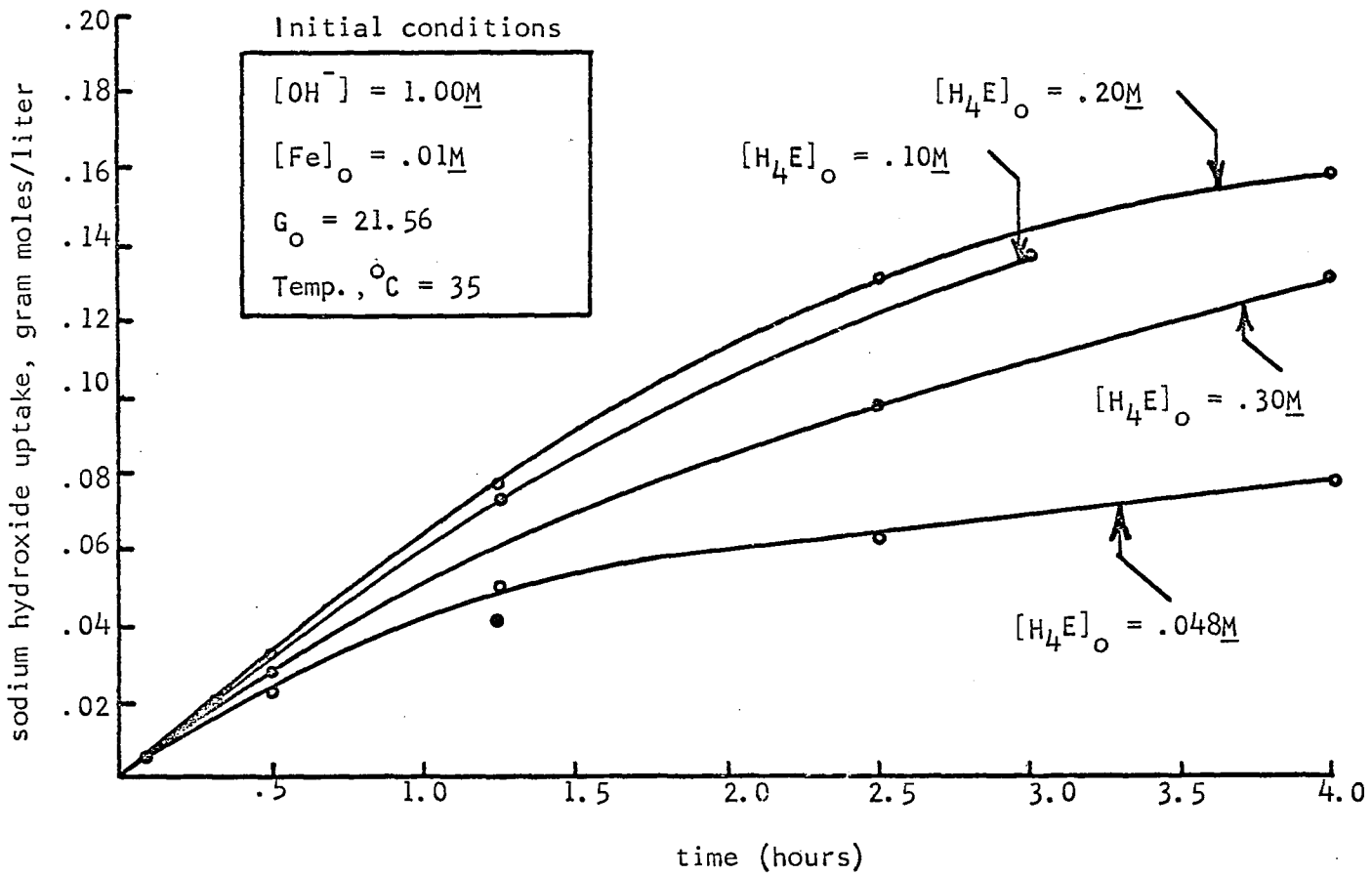


Figure (V-XI)

The effect of erythritol concentration-sodium hydroxide uptake.

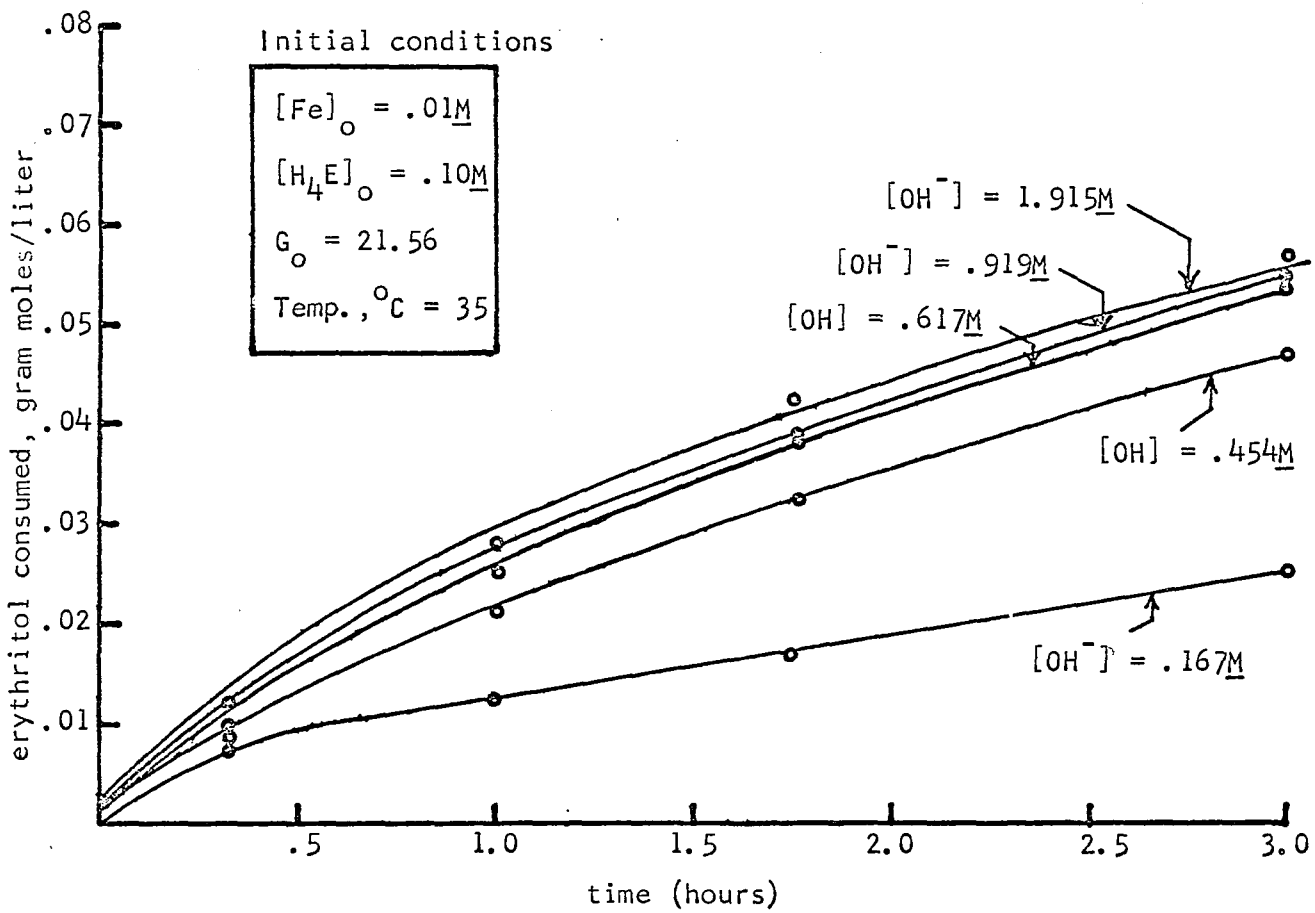


Figure (V-XII)

The effect of sodium hydroxide concentration - erythritol consumed.

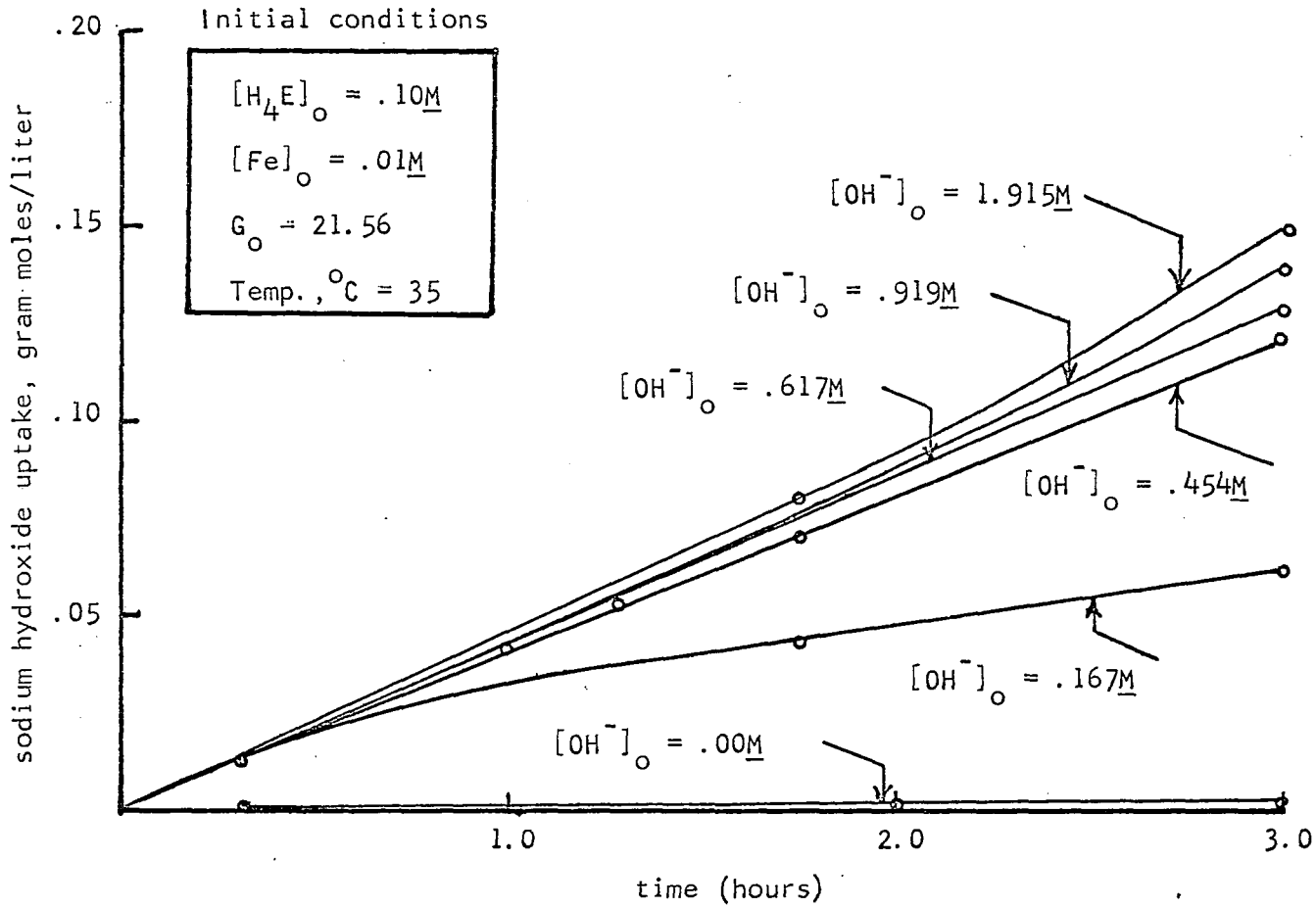


Figure (V-XIII)

The effect of sodium hydroxide concentration-alkali uptake.

G. Alkali Uptake

The alkali uptake was followed for each reaction as a function of time. Qualitatively, the results indicated that the alkali uptake curves resembled the erythritol oxidation curves when the rate was low. At high rates the alkali uptake lagged the erythritol oxidation curves. The following table gives some of the typical results obtained. The product $[Fe]_o \times [H_4E]$ is taken as a measure of the rate of reaction. This product is compared to the moles sodium hydroxide consumed per mole erythritol reacted for the entire reaction.

Run Number	Total Moles Hydroxyl Uptake / Moles Erythritol Consumed	$[Fe]_o \times [H_4E]_o \times 10^4$
16	3.25	1.08
24	2.72	4.82
14	2.40	9.95
26	1.489	20.00
27	.946	30.0

H. Material Balances

Two tests were made to determine the product distribution. The results are shown in Tables (V-I) and (V-II) and Figures (V-XIV) and (V-XV). There was some uncertainty in the "K" value assigned for the determination of the second peak for glyceric acid. For Run E-37, the

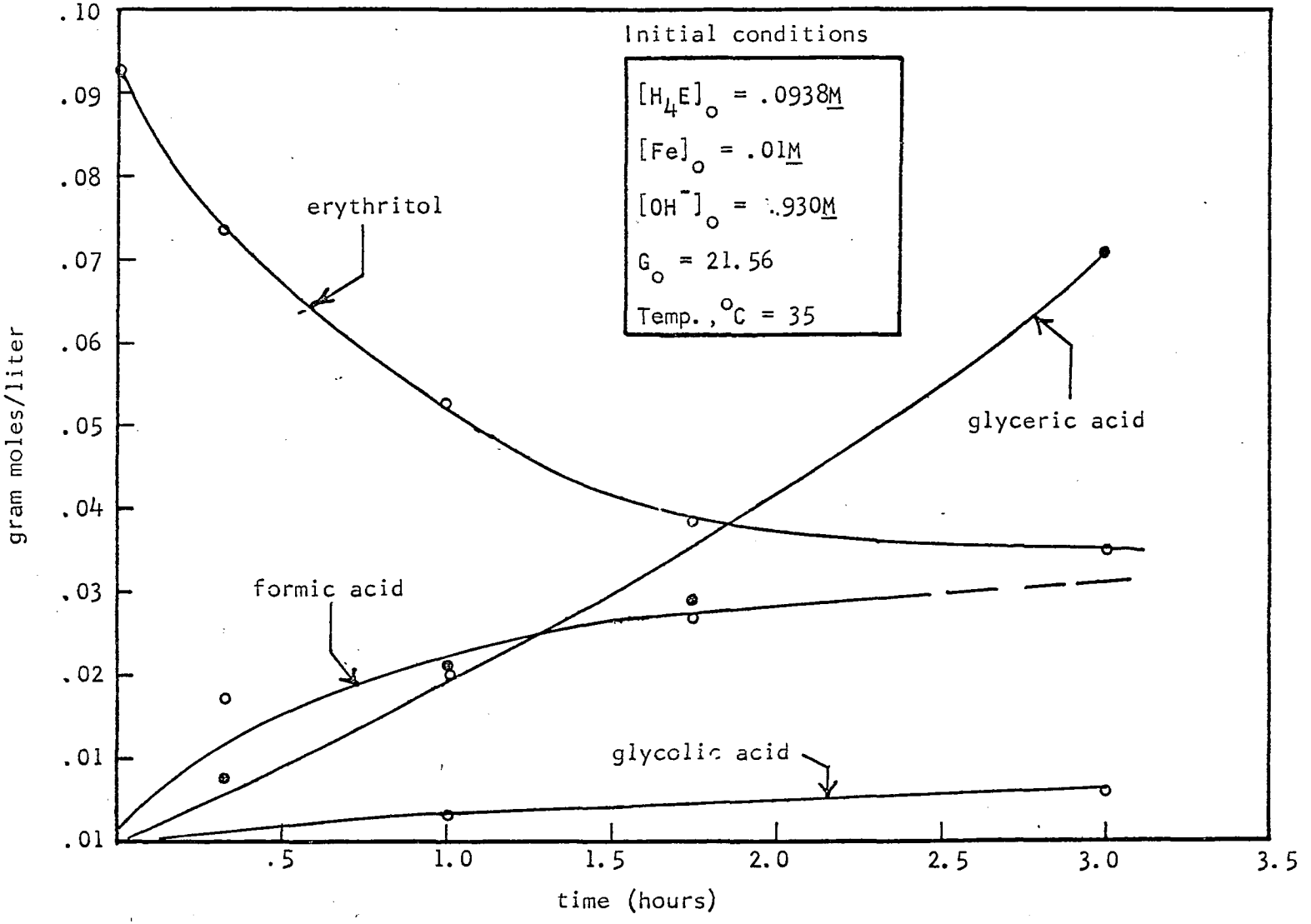


Figure (V-XIV)

Product distribution for Run E-34.

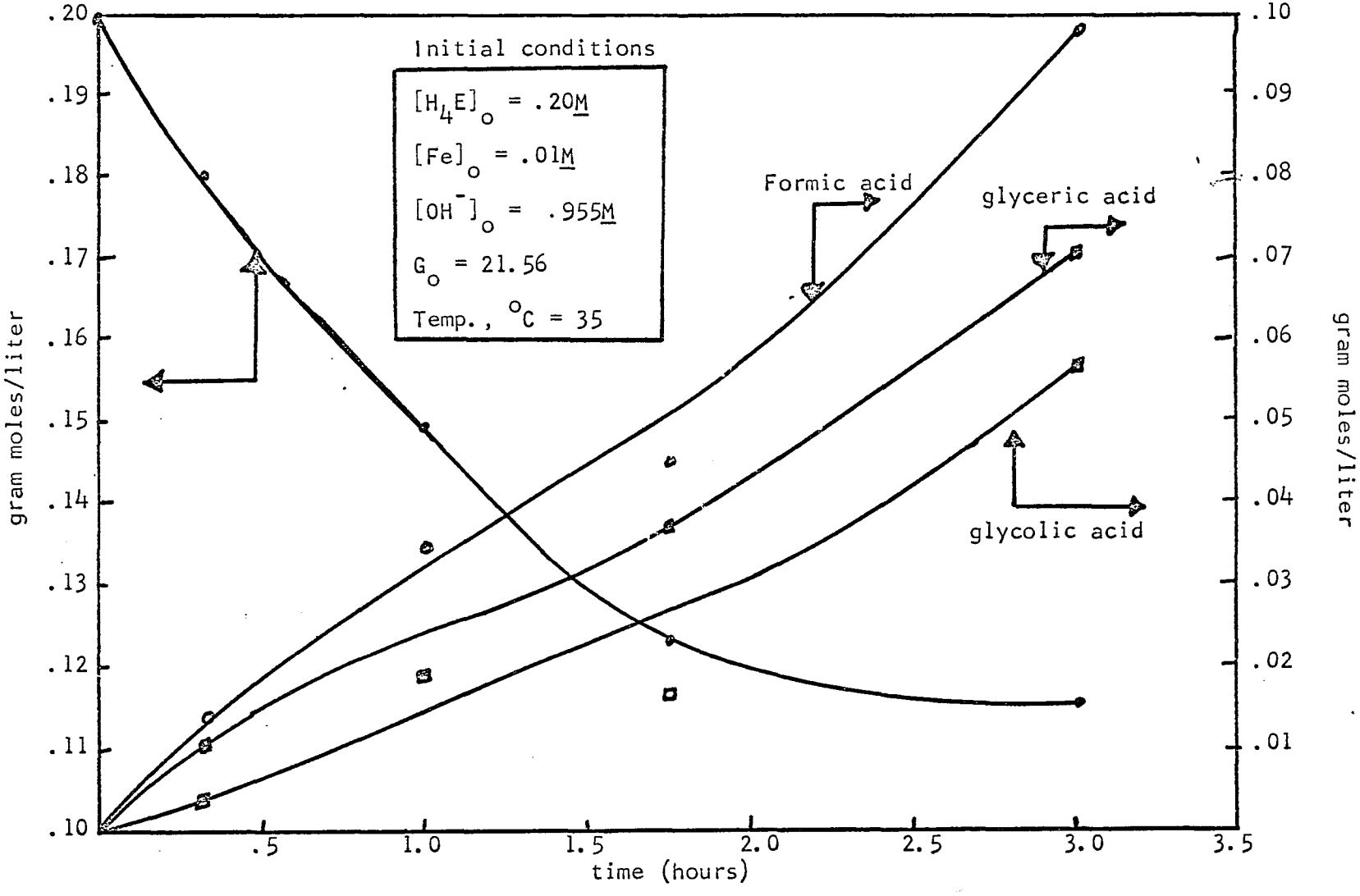


Figure (V-XV)

Product distribution for Run E-37.

Table (V-I)

Product Distribution For Oxidation of Erythritol*

Compound	Concentration Moles/Liter	Concentration .33 hours	Concentration 1.00 hours	Concentration 1.75 hours	Final Concentration 3.00 hours
Erythritol	.0934	.0736	.0528	.0385	.0349
Glyceric acid	.00	.00785	.0210	.0291	.0706
Glycolic acid	.00	.000	.00286	-	.0051
Lactic acid	.00	.001	.001	.001	.001
Formic acid	.00	.0175	.020	.027	.024
Carbon dioxide	.018	.018	.018	.018	.018
Sodium hydroxide	.930	.916	.880	.847	.772

* Run E-34

Initial ferric chloride concentration = .01M

Air flow rate = 21.56 lbs./hrs.-ft.^{2}

Initial erythritol concentration = .0934M

Table (V-11)

Product Distribution For Oxidation of Erythritol*

Compound	Concentration Moles/Liter	Concentration .33 hours	Concentration 1.00 hours	Concentration 1.75 hours	Final Concentration 3.00 hours
Erythritol	.20	.180	.149	.123	.116
Glyceric acid	.00	.0101	.0246	.03647	.0707
Glycolic acid	.00	.00298	.0188	.0162	.0567
Lactic acid	.00	.00	.00	.00	.00
Formic acid	.00	.0138	.0347	.0455	.0982
Carbon dioxide	.00	.011	.0118	.0385	.0294
Sodium hydroxide	.955	.921	.889	.849	.789

* Run E-37

Initial ferric chloride concentration = .01M

Air flow rate = 21.56 lbs./hrs.-ft.^{2}

Initial erythritol concentration = .20M

erythritol concentration was calculated by considering the fractional change in the Φ value for erythritol.

1. Ion Exchange Tests

Ten ml. samples containing erythritol and sodium hydroxide were tested in the presence and the absence of ferric chloride to see if direct treatment of the product solution with an anion exchange resin would remove the erythritol as a complex. The characteristic color of the ferric ion was removed with the anion exchange resin. The following results were obtained.

Direct Treatment With IR-400
Anion Exchange Resin

	Concentration Before Treatment gram moles/liter			Concentration After Treatment
Solution Number	Erythritol	NaOH	Ferric Chloride	Erythritol
I-1	.10	1.00	.00	.108
I-2	.10	1.00	.01	.0725
I-3	.10	1.00	.03	.0712

Apparently part of the erythritol exists in solution as a negatively charged complex.

Further tests were made to see if the solution could first be treated with a cation exchange resin to break the complex and then with an anion exchange resin to remove any acids present. A solution containing only the complex was treated in this manner and the results are listed below.

Sample No.	Treatment	Final Erythritol Concentration Gram moles/liter
E-9-0*	None	.0946
E-9-0	Cation Exchange Resin IR-120	.0965
E-9-0	(1) Cation Exchange Resin IR-120 (2) Anion Exchange Resin IR-400	.0966

* Erythritol conc. = approximately .096 moles/liter

Ferric chloride conc. = .01 moles/liter

Sodium hydroxide conc. = .901 moles/liter

J. Spot Tests

Several tests were made on the product solution for specific compounds. The reagents used are listed in Appendix B.

Compound Tested For	Results	Sample Age
Formaldehyde	Negative	4 days
Formaldehyde	Positive	0
Formic acid	Positive	4 days
Lactic acid	Positive	4 days
Oxalic acid	Negative	4 days
Glyceric acid	Inconclusive	4 days
Glycolic acid	Positive	0
Glycolic acid	Positive	4 days
Aldehydes	Inconclusive	0

CHAPTER VI

DISCUSSION OF RESULTS

The results of the study are discussed and a mechanism is proposed to explain the kinetic data.

A. Mass Transfer Effects

1. Temperature

Since the reaction is a complex one, the temperature coefficient for the entire reaction has little meaning. Qualitatively, as predicted by collision theory, the rate increases with temperature in the 30 - 40°C region. (See Figure (V-IV).) Apparently, above 40°C, the rate of the reaction is so fast that it is limited by mass transfer of oxygen or some other component. The data taken at 35°C is within the "kinetic regime", if the other experimental conditions are not seriously varied.

2. Air Rate

As discussed in Chapter IV, there are three bubble regimes, $G_o = > 8.5$, $G_o \cong 8.5 - 25.0$ and $G_o > 25.0$. To test for the effect of air rate, an experimental run was made in each regime. From Figure (V-VI), it is apparent that there are apparently no mass transfer effects above $G_o = 5.46$.

B. Product Distribution

From the data in Chapter V, the major products of the reaction

are glyceric, glycolic and formic acids. A carbon balance on Run E-37 and E-34 gives the following results.

E-37

Component	Beginning Concentration	No. Carbon Atoms	Final Concentration	No. Carbon Atoms
Erythritol	.20M	.80	.116M	.464
Glyceric Acid	.00M	.00	.0707M	.2121
Glycolic Acid	.00M	.00	.0567M	.1134
Formic Acid	.00M	.00	.0982M	.0982
Carbon Dioxide	.00M	.00	.0294M	.0294
Total		.80		.917

E-34

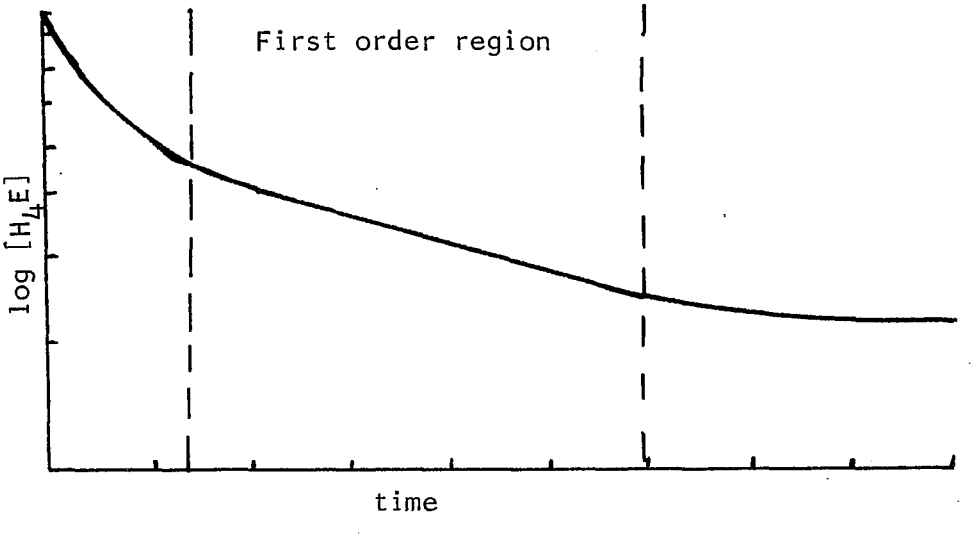
Component	Beginning Concentration	No. Carbon Atoms	Final Concentration	No. Carbon Atoms
Erythritol	.0934M	.3736	.0349M	.1396
Glyceric Acid	.00M	.00	.0706M	.2118
Glycolic Acid	.00M	.00	.0051M	.0102
Formic Acid	.00M	.00	.024M	.0240
Carbon Dioxide	.018M	.018	.018M	.018
Total		.3916		.4036

If the glycolic and glyceric acids are direct products of carbon-carbon cleavage, the data from E-37 indicate that of the erythritol reacted in that particular test, 28% was cleaved to glycolic and 62% to glyceric acid.

Spot tests of the reaction products indicated that small amounts of lactic acid were present and that oxalic acid was not present.

C. Kinetic Effects

The rate curves from the tests have a common shape. In the early part of the reaction, especially at high erythritol concentrations, there is an unsteady state period with a high rate. Following this initial region there is a period during which the rate appears to drop off approximately first order with respect to erythritol and then a later region during which the rate falls off rapidly, an apparent "catalyst poisoning effect". A representation of the usual shape of the curve is shown below.



The first period was eliminated from quantitative considerations because the extrapolated data for initial rates was not precise enough. The "first order" period was treated quantitatively to obtain the apparent first order velocity constants as a function of the various variables and the third period is treated semi-quantiatively in section D.

1. Catalyst Concentration

The data from runs E-16 through E-20 are plotted in Figure (VI-1). The ion exchange-periodate method of analysis yields the total erythritol concentration, complexed and uncomplexed. The assumption is made that most of the erythritol is in the form of the monoerythritol-Iron(III) complex (K_{11} is small). The experimental data is adjusted so that:

$$[H_4E] = [C_E]_{\substack{\text{periodate} \\ \text{analysis}}} - [Fe]_o$$

The apparent first order velocity constants are calculated using the slopes of the curves in the "first order" period and tabulated below.

Run No.	Initial Ferric Chloride Concentration (gram moles/liter)	k_1, Apparent First Order Velocity Constant Based on Erythritol Concentration $hr.^{-1}$
E-16	.001	.10
E-17	.004	.22
E-32	.010	.294
E-19	.015	.509
E-20	.030	.8025

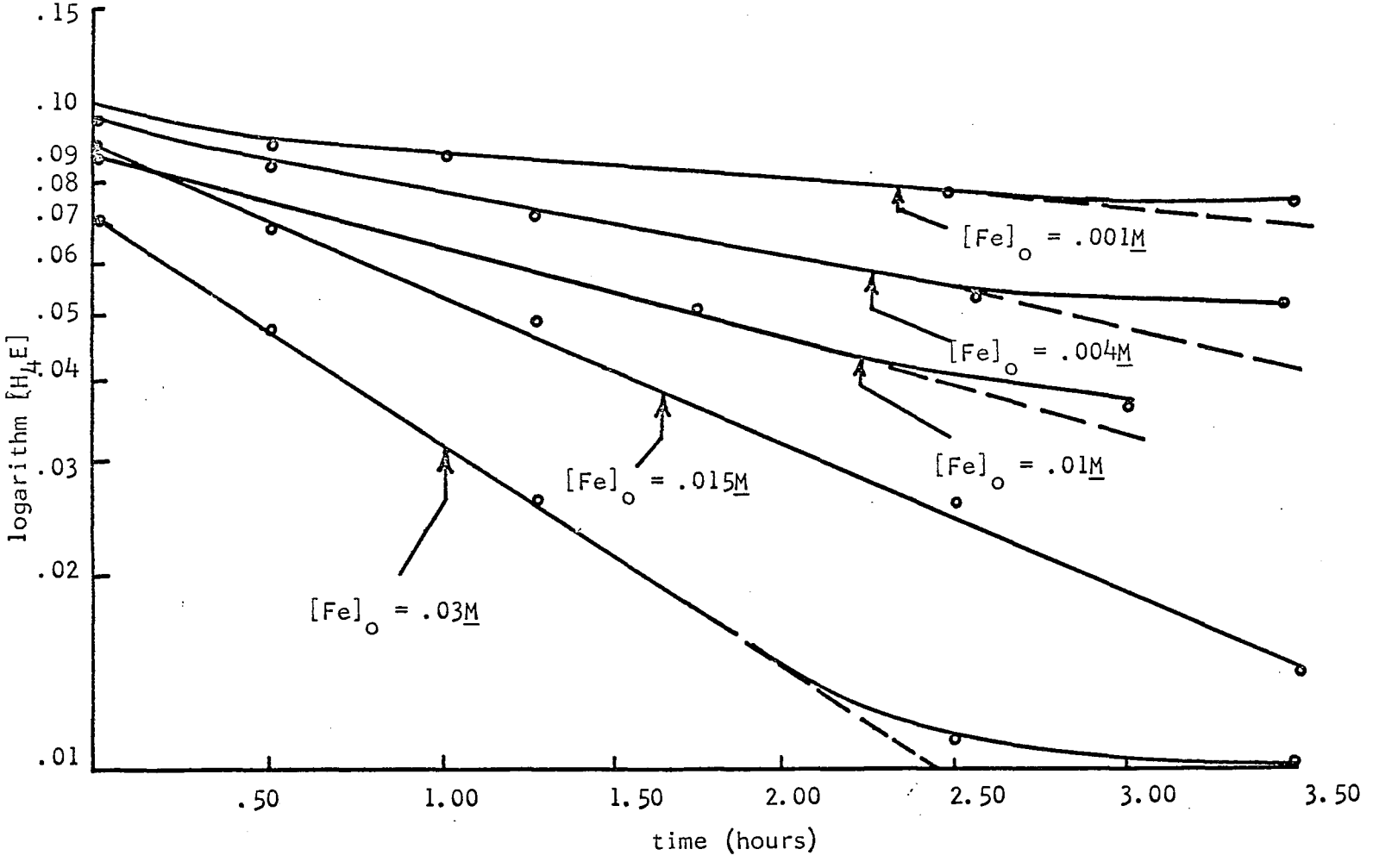


Figure (VI-1)

A plot of the logarithm of the erythritol concentration versus time as a function of the initial catalyst concentration.

The first order velocity constants* are plotted in Figure (VI-II). The variation appears to be approximately first order with respect to ferric ion concentration in the "first order" period.

2. Erythritol Concentration

The data for runs at varying initial erythritol concentrations are plotted in Figure (VI-III). The runs at low concentration appear to be approximately first order with respect to erythritol concentration.

For $[H_4E]_o = .19\underline{M}$, the "first order" period is very short and at $[H_4E]_o = .29$, the "first order" portion is non-existant.

3. pH

The reaction will not proceed to any measurable extent in the absence of hydroxyl ion. The data from runs at varying hydroxyl concentration are plotted in Figure (VI-IV). The first order velocity constants, obtained by taking the slope of straight lines drawn through the data points in the "first order" period, are tabulated below and plotted in Figure (VI-V).

---

* $$\frac{d[C_E]}{d\theta} = k_1 [H_4E] \; : \; \frac{d[C_E]}{d\theta} + \frac{d[H_4E}{d\theta} + \frac{d[Fe]_o}{d\theta} = \frac{d[H_4E]}{d\theta}$$

$$k_1 = \frac{\ln [H_4E]_2 - \ln [H_4E]_1}{\theta_2 - \theta_1}$$

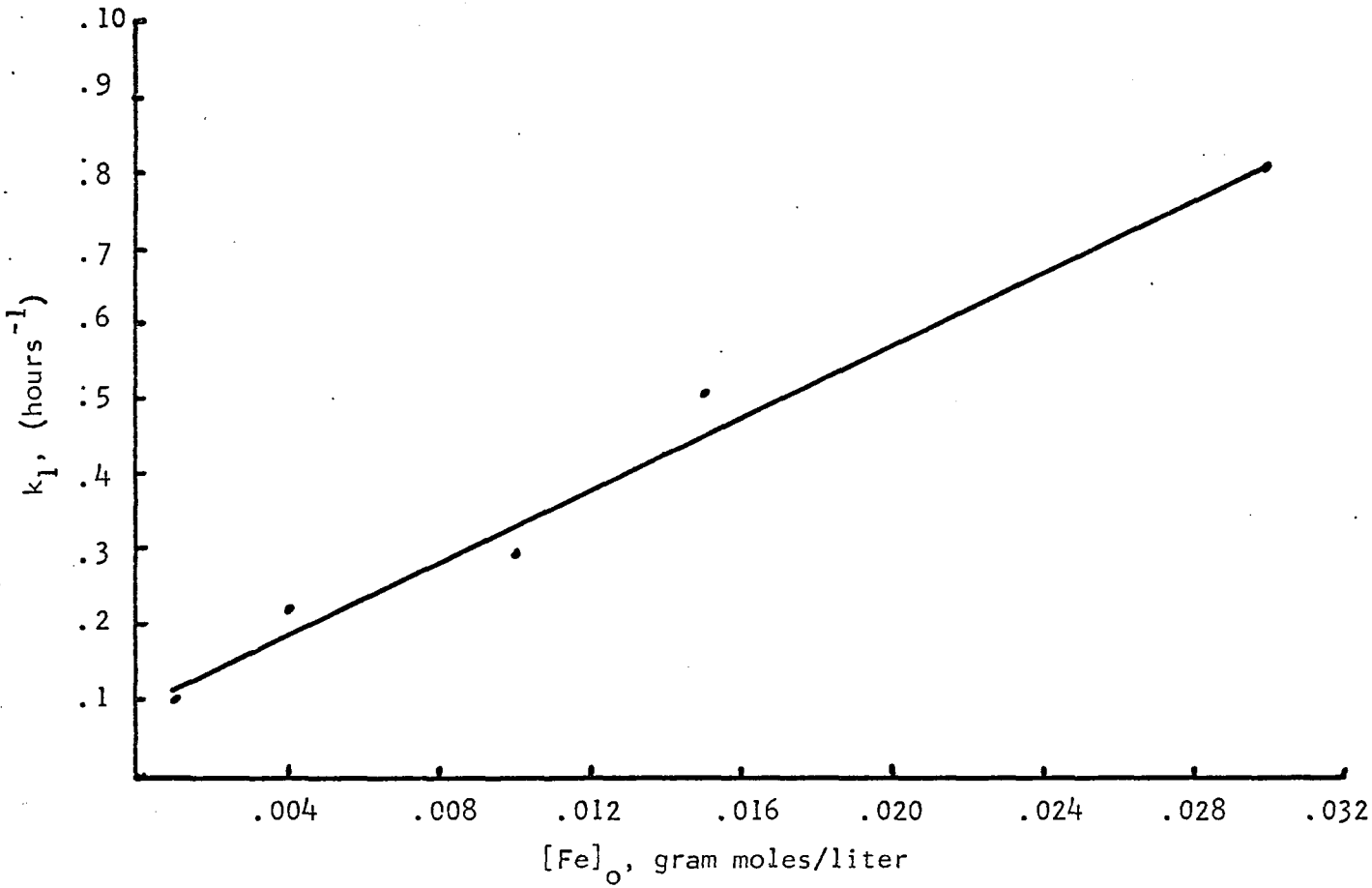


Figure (VI-11)

A plot of the average first order velocity constant, k_1, versus initial catalyst concentration.

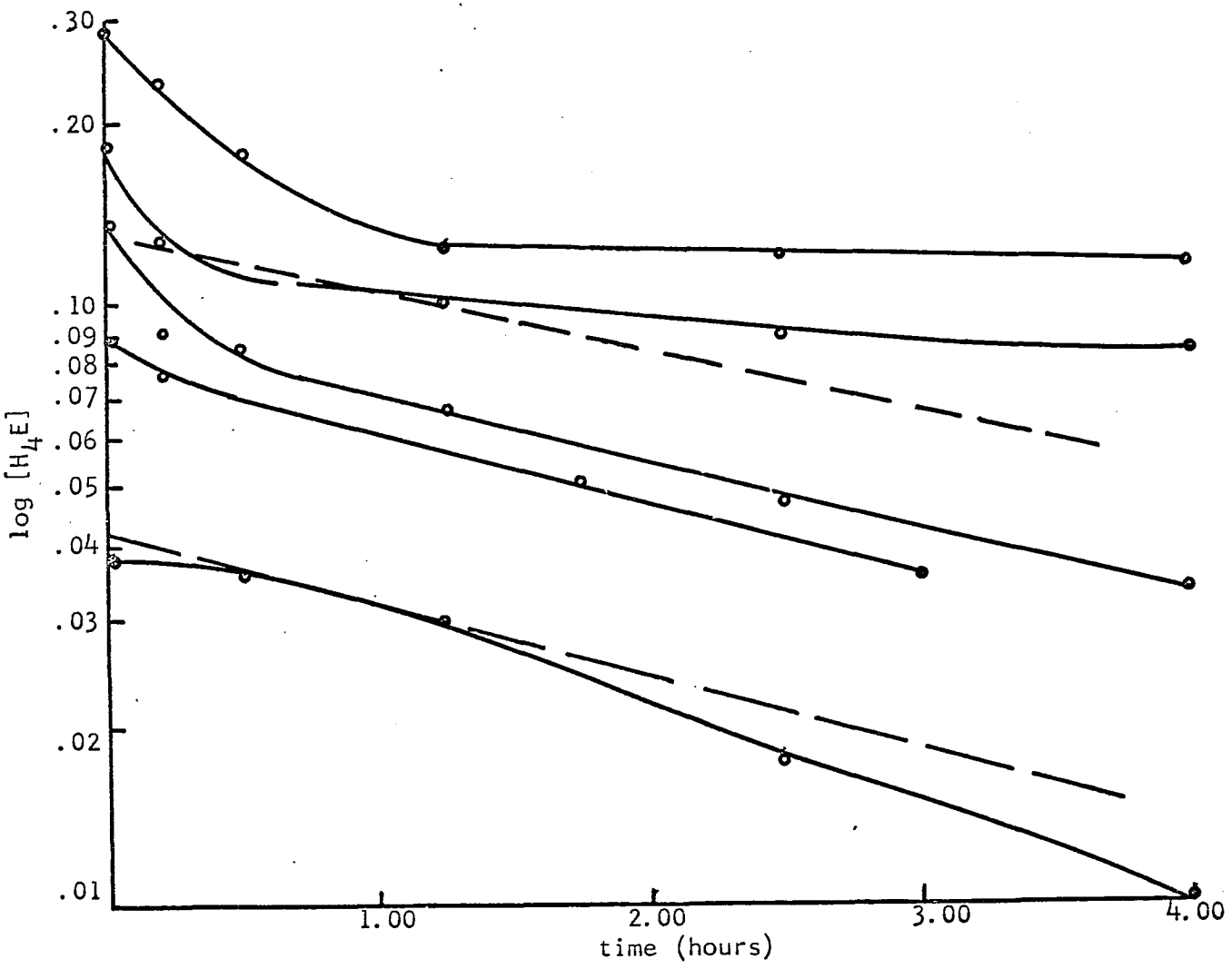


Figure (VI-III)

A plot of the logarithm of the erythritol concentration versus time as a function of initial erythritol concentration.

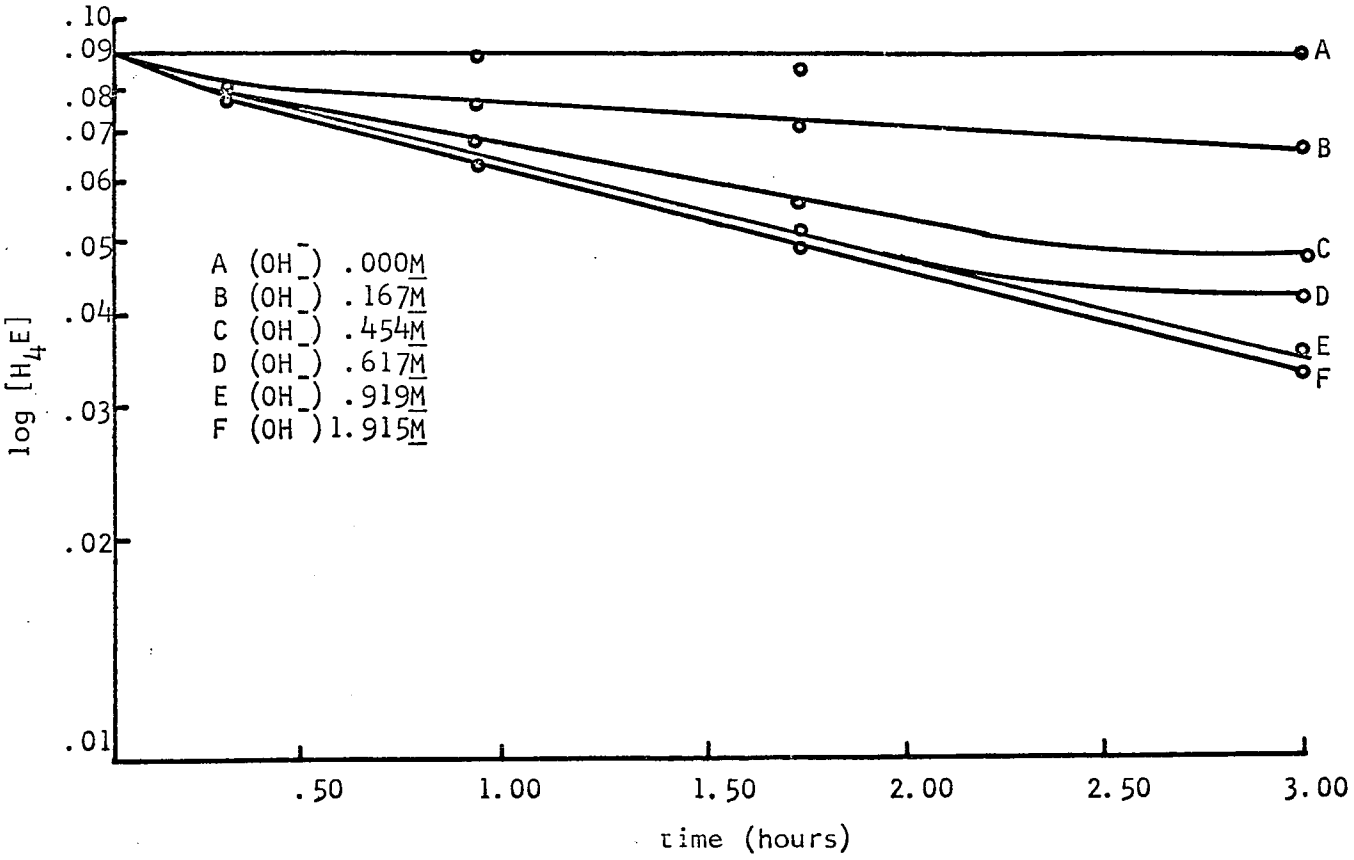


Figure (VI-IV)

A plot of the logarithm of the erythritol concentration versus time as a function of the hydroxyl ion concentration.

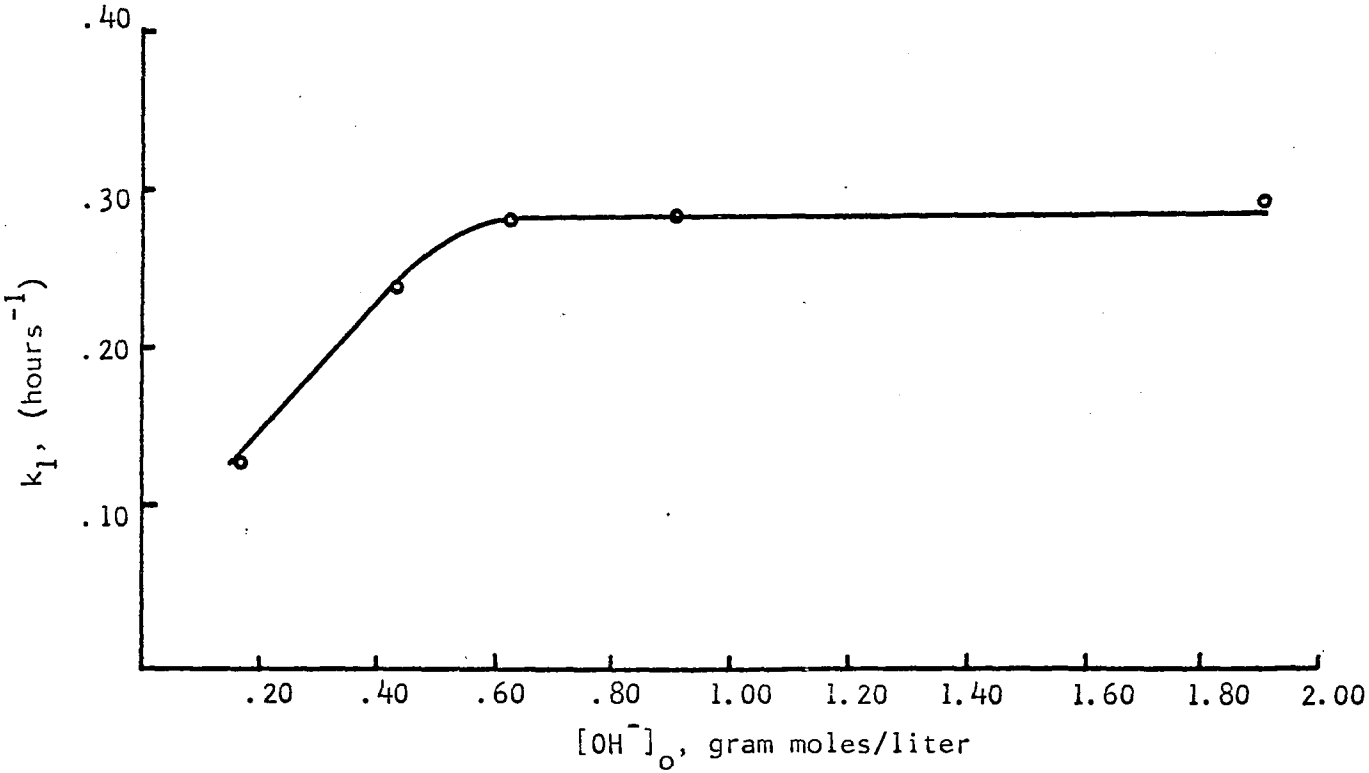


Figure (VI-V)

A plot of the first order velocity constant, k_1, versus the initial hydroxyl concentration.

Run No.	Hydroxyl Ion Concentration gram moles/liter	First Order Velocity Constant k_1, hr.$^{-2}$
E-31	.00	.00
E-30	.167	.126
E-29	.454	.243
E-33	.617	.290
E-32	.917	.290
E-28	1.915	.30

Above about .5M, the rate appears to be nearly zero order with respect to [OH] concentration.

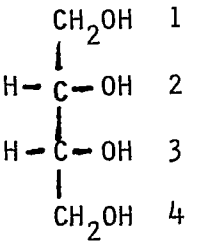
D. Proposed Mechanism

In order to explain the kinetic effects found in part (b) a kinetic mechanism and a resulting rate expression are proposed. Some speculations are also made about the molecular reactions and structures.

1. Molecular Mechanism

The reaction will not proceed to any measurable extent in the absence of a catalyst. This fact along with the non-precipitation of the ferric ion in the alkaline solution suggests that a Iron(III)-erythritol complex forms and is the oxidizable species. The concentration of such a complex should be equal or proportional to the ferric ion concentration present, since any free ferric ion would be precipitated. From these considerations, the rate of oxidation of the erythritol should be proportional to the concentration of the complex and not be linearly dependent upon the erythritol concentration. The data suggests that in effect, the reverse is true. In a range of

concentrations, the rate is nearly first order with respect to erythritol concentration. The explanation suggested here for this behavior, is the formation of two complexes between erythritol and iron, an unoxidizable mono-erythritol complex and an oxidizable di-erythritol complex. As seen from the product distribution however, both glyceric and glycolic acid are formed, indicating that the cleavage can occur either between carbons 1 and 2 or 2 and 3.



The di-erythritol complex may then have two forms, depending on whether the Iron(III) is complexed between carbons 1 and 2 or 2 and 3. The complexes formed undergo disproportionation reactions to intermediate products that are then oxidized to glycolic, glyceric and formic acids. The reactions may occur as shown in Figures (VI-VI) and (VI-VII).

2. Kinetic Mechanism

The complex formation equations and the corresponding disproportionation reactions may be written as follows:

$$H_4E + Fe^{+++}_{OH,H_2O} + OH^- \rightleftarrows \underset{I}{Fe(H_2E)^-} + 3H_2O \qquad 6.1$$

$$Fe(H_2E)^- + H_4E \rightleftarrows \underset{II}{Fe(H_2E)_2^-} + 2H_2O \qquad 6.2$$

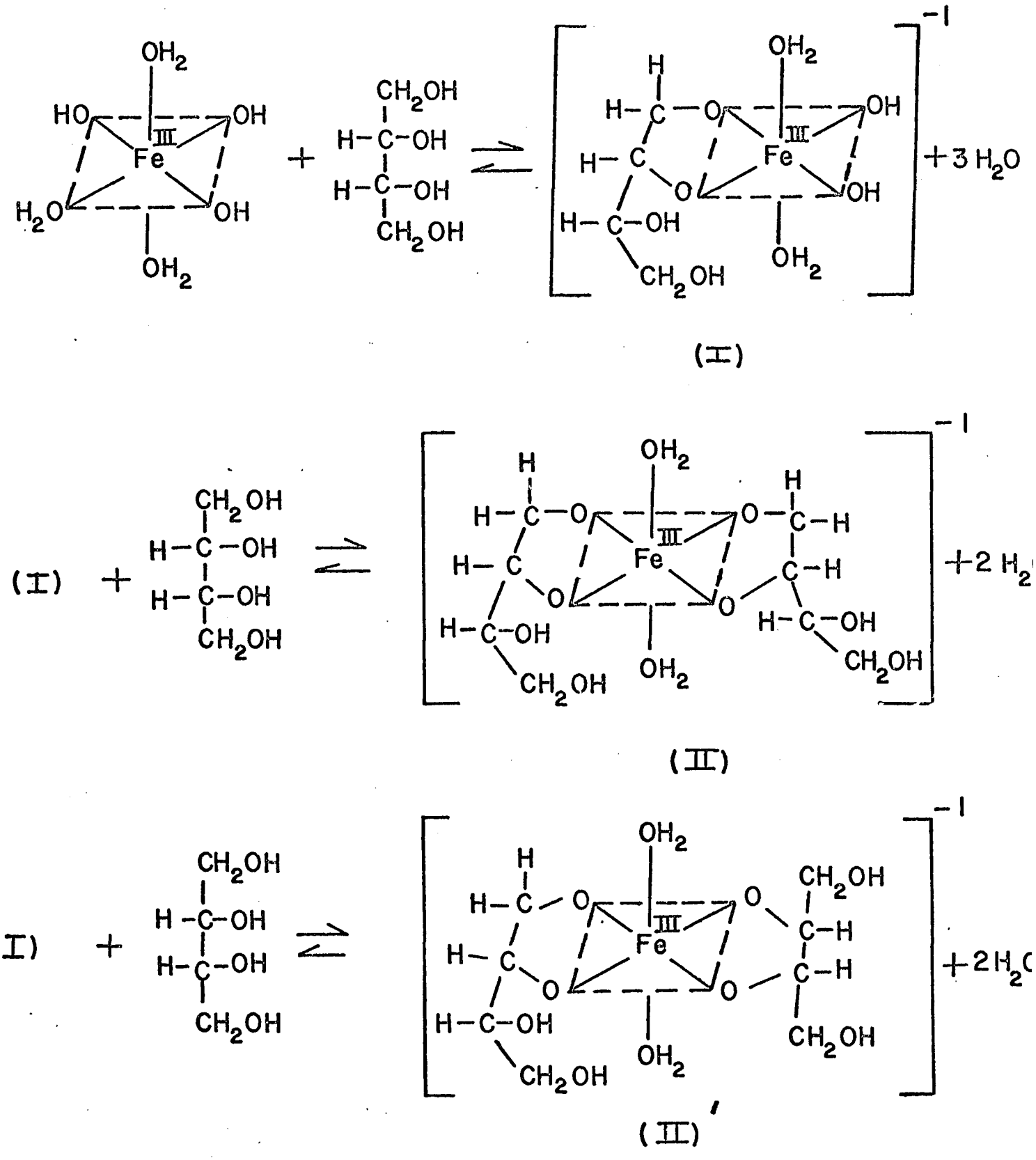
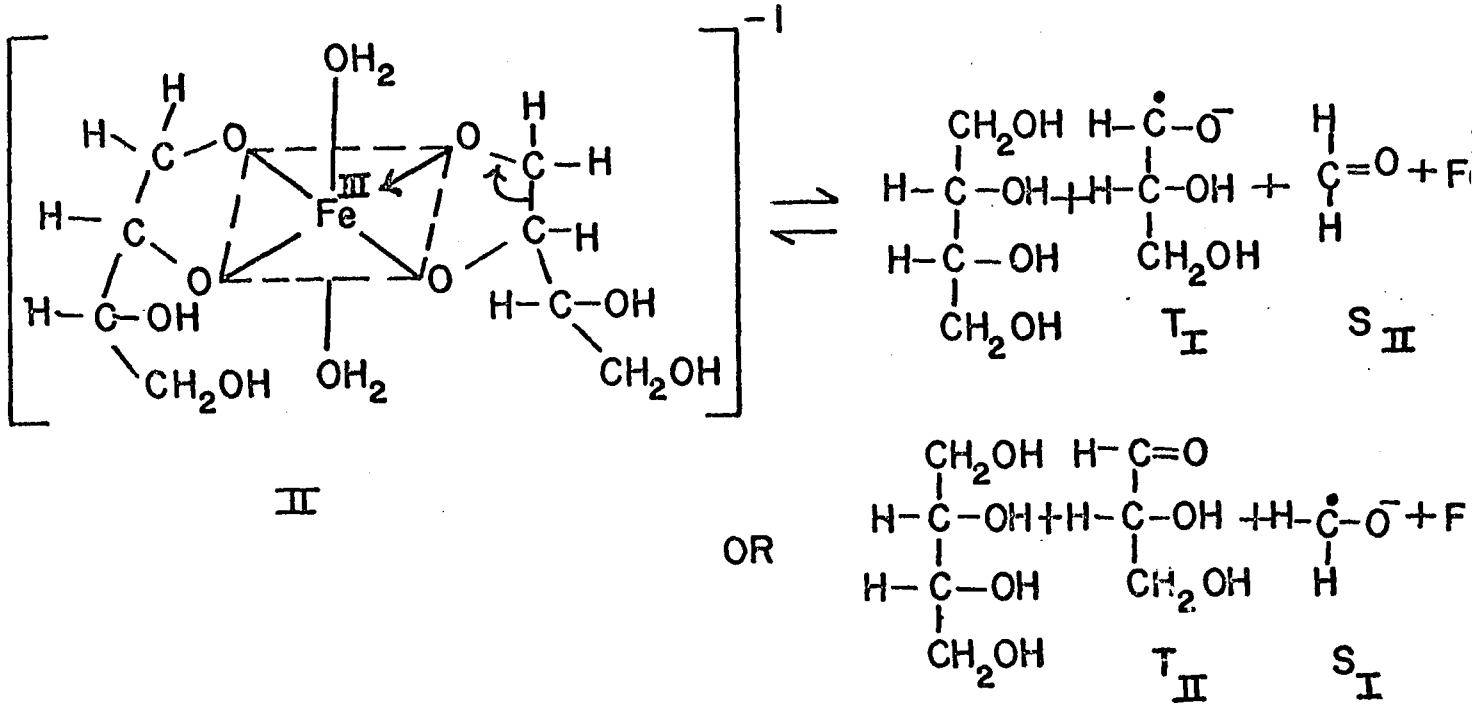


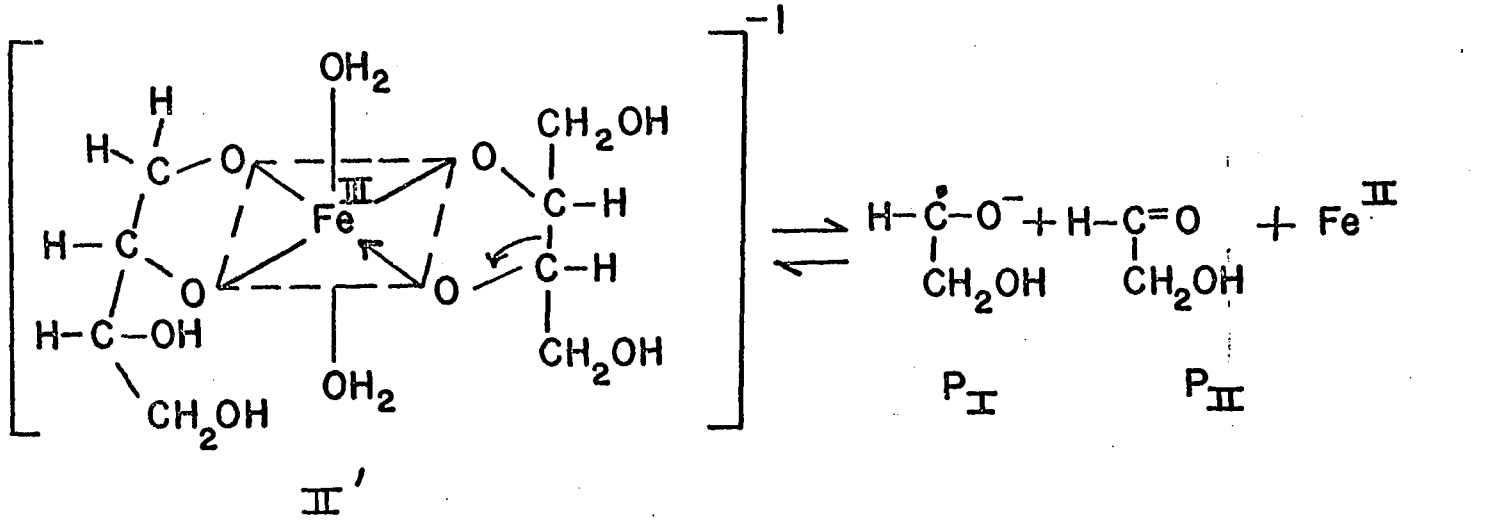
Figure (VI-VI)

Formation of chelate compounds.



II

OR



II'

Figure (VI-VII)

Disproportionation of reactive chelate compounds.

$$Fe(H_2E)^- + H_4E \underset{}{\overset{\rightarrow}{\leftarrow}} Fe'(H_2E)_2^- + 2H_2O \qquad 6.3$$

II'

$$Fe(H_2E)_2^- \rightarrow Fe^{+2} + H_4E + S + T \qquad 6.4$$

II

$$Fe'(H_2E)_2^- \rightarrow Fe^{+2} + H_4E + 2\,P \qquad 6.5$$

II'

The corresponding stability constants for the complexes are,

$$K_I = \frac{[Fe(H_2E)^-]}{[H_4E][Fe^{+++}_{OH,H_2O}][OH^-]} \qquad 6.6$$

$$K_{II} = \frac{[Fe(H_2E)_2^-]}{[Fe(H_2E)^-][H_4E]} \qquad 6.7$$

$$K_{II'} = \frac{[Fe'(H_2E)_2^-]}{[Fe(H_2E)^-][H_4E]} \qquad 6.8$$

The rate of disappearance of erythritol would be:

$$\frac{-d[C_E]}{d\theta} = k_1\,[Fe(H_2E)_2^-] + k_2\,[Fe'(H_2E)_2^-] \qquad 6.9$$

II II'

It can be shown (see Appendix F) that Equation 6.9 can be written:

$$\frac{-d[C_E]}{d\theta} = k' \, [Fe(H_2E)_2^-]_{Total} \qquad 6.9'$$

where;

$$k' = \frac{k_1 K_{II} + k_2 K_{II'}}{K_{II} + K_{II'}}$$

and

$$[Fe(H_2E)_2^-]_{Total} = [Fe(H_2E)_2^-] + [Fe'(H_2E)_2^-]$$

The data indicates that the rate of hydroxyl uptake often lags the rate of reaction, especially at high reaction rates, suggesting a finite lifetime for some of the oxygen unsaturated products. It has also been shown in Chapter III that the products of one equivalent reaction are often an aldehyde and a radical anion. Products S, T and P might then be oxygen unsaturated intermediates that react further with some of the following reactions. Since the major reaction products are formic, glyceric and glycolic acid it is possible that S, T and P are the corresponding aldehydes or radical anions shown in Figures (VI-VI) and (VI-VII).

$$T_{II} + 1/2\ O_2 + OH^- \rightleftharpoons H - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - \underset{OH}{C}\overset{O}{\overset{\|}{}} + H_2O \qquad 6.15$$

$$T_1 + Fe^{+2} + O_2 \rightleftharpoons OH^- + H - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{H}{C}} - \underset{OH}{\overset{O}{C}} + Fe^{+3} \qquad 6.16$$

(Plus corresponding reactions for S and P)

The ferrous ions produced by Equations 6.4 and 6.5 are probably oxidized by molecular oxygen to the ferric state. The oxidation potential of the reaction is very favorable for the reaction and the rate is very high.

$$Fe^{+2} + O_2 \overset{\text{fast}}{\rightleftharpoons} Fe^{+3} + O_2^- \qquad 6.17$$

In order to simplify the rate equation, an expression for $[Fe(H_2E)_2^-]$ must be obtained.

From Equations 6.7 and 6.8

$$[Fe(H_2E)_2^-] = K_{II}\,[Fe(H_2E)^-][H_4E] \qquad 6.18$$

$$[Fe'(H_2E)_2^-] = K'_{II}\,[Fe(H_2E)^-][H_4E] \qquad 6.19$$

adding together

$$[Fe(H_2E)_2^-] + [Fe'(H_2E)_2] = [Fe(H_2E)_2^-]_{Total} = [K_{II} + K'_{II}][Fe(H_2E)^-][H_4E] \qquad 6.20$$

The effective Iron(III) concentration concentration available for chelation is distributed between the two complexes and the following

relationship holds.

$$[Fe]_o = [Fe(H_2E)_2^-]_{Total} + [Fe(H_2E)^-] \qquad 6.21$$

Solving for $[Fe(H_2E)^-]$ and substituting into Equation 6.20 above:

$$[Fe(H_2E)_2^-]_{Total} = [K_{II} + K'_{II}]\ \{[Fe]_o - [Fe(H_2E)_2^-]_{Total}\}[H_4E] \qquad 6.22$$

Solving for $\{Fe(H_2E)_2^-\}_{Total}$ and substituting into 6.9', the expression for the rate of oxidation of erythritol is,

$$\frac{-d[C_E]}{d\theta} = \frac{k' K_{II} [Fe]_o [H_4E]}{1 + K''_{II} [H_4E]} \qquad 6.23$$

where

$$k' = \frac{k_1 K_{II} + k_2 K'_{II}}{K_{II} + K'_{II}} \quad ;$$

$$K''_{II} = K_{II} + K'_{II}$$

The experimental data indicates a rapid fall off in the rate as the reaction proceeds. The rate fall off might be predicted because of the chelate forming ability of the glyceric (HGe) and glycolic (HGo) acids formed in the reaction, thus reducing the effective ferric ion concentration.

The equilibrium constants for the acid dissociation of glyceric and glycolic acid are $10^{3.52}$ and $10^{3.72}$ respectively and thus in basic solution would probably be completely dissociated into the ionized species. The following equations then might represent the chelation reactions.

$$Ge^{-} + Fe^{+++}_{OH,H_2O} \rightleftharpoons Fe(Ge)^{-1} + H_2O \qquad 6.24$$

$$Go^{-} + Fe^{+++}_{OH,H_2O} \rightleftharpoons Fe(Go)^{-1} + H_2O \qquad 6.25$$

The multiacid chelates such as $Fe(Ge)_2^{-1}$ could also form but their contribution, if any, could be added.

The corresponding stability equations for the chelates would be as follows

$$(k_1)_{Ge} = \frac{[Fe(Ge)^{-1}]}{[Ge^{-}][Fe^{+++}]} \qquad 6.26$$

$$(k_1)_{Go} = \frac{[Fe(Go)^{-1}]}{[Go^{-}][Fe^{+++}]} \qquad 6.27$$

$(k_1)_{Go}$ has been reported[1,2] as 4.71 and $(k_1)_{Ge}$ would be expected to have the same order of magnitude.

Lactic acid was detected in some runs and under prolonged oxidation oxalic acid has been found.[9] Acid dissociation and stability constants for other possible reaction products are tabulated in Table (VI-1).

Table (VI-1)

Acid Dissociation and Stability Constants for Iron(III)

Chelates of Possible Reaction Products

Acid	Acid Dissociation Constant, Log K	Ionic Strength	Temperature °C	Iron(III)-Chelate Stability Constants	Reference
Lactic	3.74 (pk_1)	.2	-	-	3,4
Lactic	-	-	-	6.4 (k_1)	1,2
Glycolic	3.71)pk_1)	.2	-	-	3,4
Glycolic	-	-	-	4.71 (k_1)	1,2
Glyceric	3.52 (pk_1)	.2	-	-	3,4
Oxalic	1.24 (pk_1)	0	25	-	3,5
	4.14 (pk_2)	-	25		3,5
Oxalic	-	0	25	10 (k_1)	3,6
				18 ($k_1 x k_2 x k_3$)	3,7
Tartartic	3.94 (pk_1)	.2			1,4
	2.88 (pk_2)	.2			1,4

The ferric ion concentration available for chelation with erythritol would then be reduced by the amount involved in the chelation reactions with the reaction products.

$$[Fe]_o = [Fe]_o - \Sigma [Fe\ HK] \qquad 6.28$$

where HK = acid products

The corrected expression considering the self poisoning effect of the acid products can be derived as follows, making a material balance on the ferric ion,

$$[Fe]_o = [Fe(H_2E)_2^-]_{Total} + [Fe(H_2E)^-] + [FeGe^-] + [FeGo^-] \qquad 6.29$$

From the stability constants of the complexes, and the ionization constants of the acids, we know that;

$$[Fe^{+++}] = \frac{[Fe(H_2E)^-]}{K_1[H_4E][OH^-]} = \frac{[Fe(Ge)^{-1}][K_1]_{Ge}[Kw]}{[HGe][OH^-][k_1]_{Ge}} =$$

$$= \frac{[Fe(Go)^{-1}][K_1]_{Go}[Kw]}{[HGo][OH^-][k_1]_{Go}} \qquad 6.30$$

Solving for $[Fe(Ge)^{-1}]$ and $[Fe(Go)^{-1}]$,

$$[Fe(Ge)^{-1}] = \frac{[Fe(H_2E)^-][HGe][k_1]_{Ge}}{[K_1][K_1]_{Ge}[Kw][H_4E]} \qquad 6.31$$

$$[Fe(Go)^{-1}] = \frac{[Fe(H_2E)^-][HGo][k_1]_{Go}}{[K_1][K_1]_{Go}[Kw][H_4E]} \qquad 6.32$$

Substituting into Equation 6.29,

$$[Fe]_o = [Fe(H_2E)_2^-]_{Total} + [Fe(H_2E)^-] + \frac{[Fe(H_2E)^-][HGe][k_1]_{Ge}}{[K_1][K_1]_{Ge}[Kw][H_4E]} +$$

$$\frac{[Fe(H_2E)^-][HGo][k_1]_{Go}}{[K_1][K_1]_{Go}[Kw][H_4E]} \qquad 6.33$$

Solving for $[Fe(H_2E)^-]$;

$$[Fe(H_2E)^-] = \frac{[Fe]_o - [Fe(H_2E)_2^-]_{Total}}{1 + \frac{[HGe][k_1]_{Ge}}{[K_1][K_1]_{Ge}[Kw][H_4E]} + \frac{[HG_o][k_1]_{Go}}{[K_1][K_1]_{Go}[Kw][H_4E]}} \qquad 6.34$$

Letting, $A = 1 + \frac{[HGe][k_1]_{Ge}}{[K_1][K_1]_{Ge}[Kw][H_4E]} + \frac{[HGo][k_1]_{Go}}{[K_1][K_1]_{Go}[Kw][H_4E]}$, and

substituting into Equation 6.20, the following equation results.

$$K_{11}^{II} = \frac{[Fe(H_2E)_2^-]_{Total}}{[H_4E]\ \frac{[Fe]_o - [Fe(H_2E)_2^-]_{Total}}{A}} \qquad 6.35$$

Equation 6.35 is then solved for $[Fe(H_2E)_2^-]_{Total}$,

$$[Fe(H_2E)_2^-]_{Total} = \frac{K''_{11}\ [H_4E][Fe]_o}{A + K''_{11}\ [H_4E]}$$

From Equation 6.9' the corrected rate expression for the oxidation of erythritol becomes,

$$\frac{-d[C_E]}{d\theta} = \frac{k'\ K''_{11}\ [H_4E][Fe]_o}{A + K''_{11}\ [H_4E]} \qquad 6.36$$

where;

$$A = 1 + \frac{[HGo][k_1]_{Go}}{[K_1][K_1]_{Go}[Kw][H_4E]} + \frac{[HGe][k_1]_{Ge}}{K_1[K_1]_{Ge}[Kw][H_4E]} \qquad 6.37$$

or in the more general case,

$$A = 1 + \frac{1}{[K_1][H_4E]Kw]} \ \Sigma\ \frac{[HK][k_1]_{K^-}}{[K_1]_{HK}} \qquad 6.38$$

In the absence of any interfering products, A = 1 and the equation reduces to 6.23.

E. Special Tests

In order to test the proposed mechanism several special tests were made.

1. Test for Ferrous Ions

Run E-36 was made in which some α, α'-dipridyl was added to the solution. The solution was .10M, .01M and 1.0M respectively in erythritol, ferric ion and sodium hydroxide. Control tests had shown that in the presence of even a minute amount of ferrous ion, the characteristic red color of the ferrous ion complex appeared. There was no red color during the sparging. If the sparging ceased, the red color appeared in two or three minutes. The color disappeared after one or two minutes of sparging. The results tend to support the theory that the reaction involves the oxidation and reduction of the iron and that the oxygen serves to keep the iron in the ferric state. The red color appeared in about 24 hours in a sample of the initial solution in which some α, α' dipridyl had been added.

2. Inhibition

In run E-35, some glyceric acid was added to see if the acid would inhibit the reaction. The reaction solution was .08M, .135M, .01M and .994M in glyceric acid, erythritol, ferric chloride and sodium hydroxide. The reaction was almost totally inhibited tending to support the theory that the "catalyst poisoning" is due to chelation between the ferric ion and the acid products. (See Figure (VI-VIII).)

3. Test for Formaldehyde

Some tests were made on the products to see if formaldehyde is present in the reaction solution during the reaction. Samples were taken from the reaction solution and immediately tested. Formaldehyde was found to be present in samples immediately taken. Tests on products

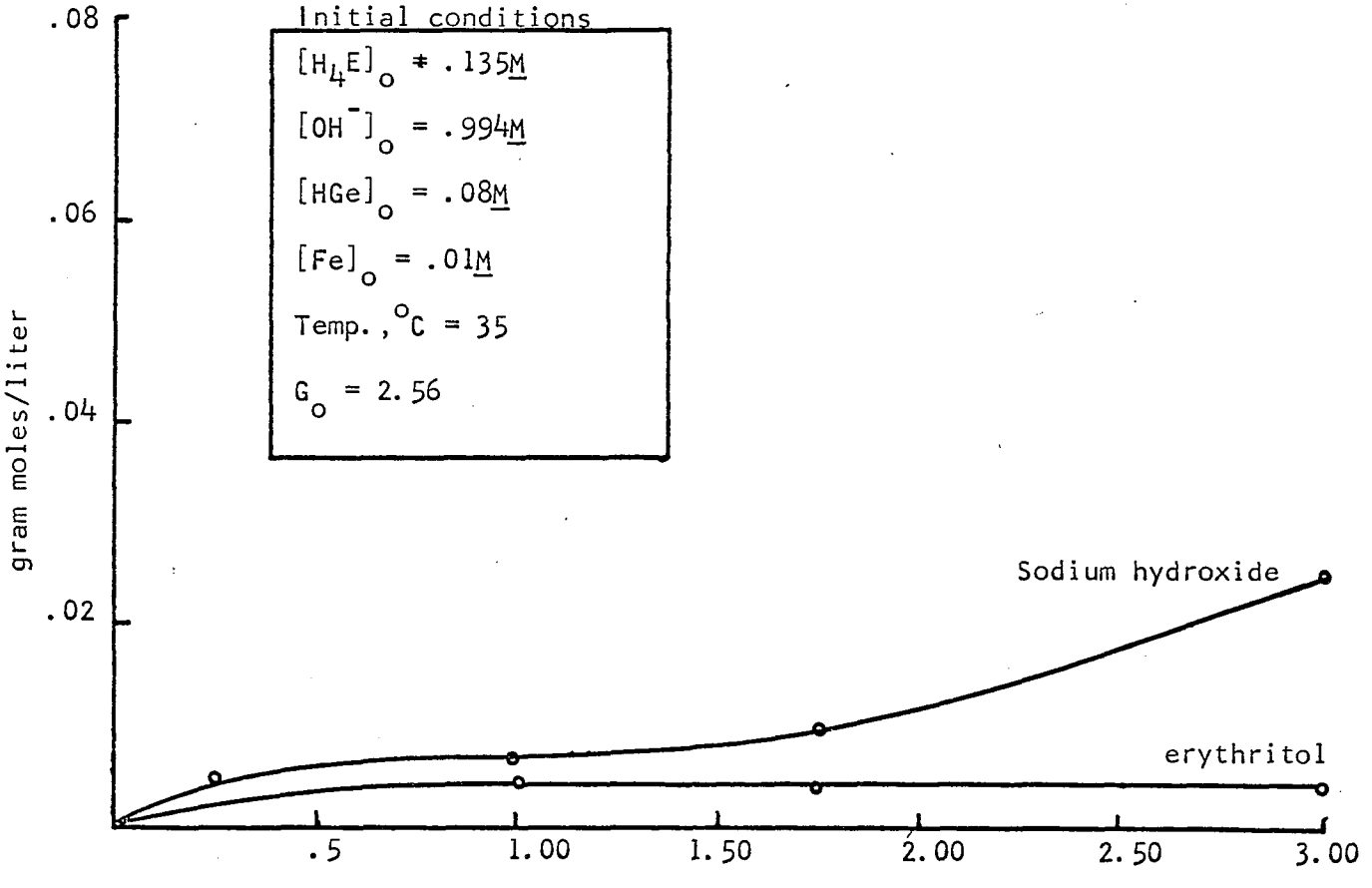


Figure (VI-VIII)

Erythritol and sodium hydroxide consumed for inhibited run, E-35.

that had been stored for a week or more gave a negative result. The presence of formaldehyde and other oxygen saturated compound could explain the lag between the erythritol reacted and the hydroxide consumed at high reaction rates.

F. Summary

The mechanism and the resulting rate expressions are summarized in Table (VI-II). The resulting rate expression is consistent with the experimental results as outlined below.

1. The rate of reaction is negligible in the absence of catalyst. The formation of erythritol-Iron(III) complexes, that are more susceptible to oxidation than erythritol, is predicted by the mechanism.

2. The rate is first order with respect to catalyst concentration. Expression 6.23 predicts a simple first order dependence on $[Fe]_o$ (before the catalyst becomes deactivated).

3. The rate is independent of the $[OH^-]$ concentration above .5M. The mechanism suggests that $[OH^-]$ is necessary for the formation of the complexes, but the derived expression does not show dependence on $[OH^-]$.

4. The reaction will not proceed in the absence of $[OH^-]$. The complexes will not form without the hydroxyl ion.

5. The rate is first order with respect to erythritol concentration at low values. The rate expression predicts first order behavior for the rate if the term $K''_{11}\ [H_4E]$ is small. The first order dependence results from the presence of two complexes, one oxidizable and one essentially unoxidizable.

Table (VI-II)

Summary of Equations for the Proposed Mechanism

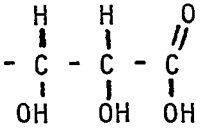
1. $H_4E + Fe^{++}_{OH,H_2O} + OH^- \rightleftarrows Fe(H_2E)^- + H_2O$ K_I

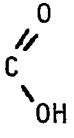
2. $Fe(H_2E)^- + H_4E \rightleftarrows Fe(H_2E)_2^- + 2\ H_2O$ K_{II}

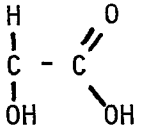
3. $Fe(H_2E)^- + H_4E \rightleftarrows Fe'(H_2E)_2^- + 2\ H_2O$ K'_{II}

4. $Fe(H_2E)_2^- \rightarrow Fe^{+2} + H_4E + S + T$

5. $Fe'(H_2E)_2^- \rightarrow Fe^{+2} + H_4E + 2\ P$

6. $T + 1/2\ O_2 + \rightleftarrows$  (HGe)

7. $S + 1/2\ O_2 + OH^- \rightleftarrows$ 

8. $P + 1/2\ O_2 + OH^- \rightleftarrows$  (HGo)

9. $Fe^{+2} + O_2 \rightleftarrows Fe^{+++} + O_2^-$

10. $HGe + OH^- \rightleftarrows Ge^- + H_2O$ $[K_I]_{Ge}$

11. $Ge^- + Fe^{+++}_{OH,H_2O} \rightleftarrows Fe(Ge)^{-1} + H_2O$ $[k_1]_{Ge}$

12. $HGo + OH^- \rightleftarrows Go^- + H_2O$ $[K_I]_{Go}$

13. $Go^- + Fe^{+++}_{OH,H_2O} \rightleftarrows Fe(Go)^{-1} + H_2O$ $[k_I]_{Go}$

Final Rate Expression

$$\frac{-d[C_E]}{d\theta} = \frac{k'K'_{II}\,[H_4E][Fe]_o}{A + K'_{II}\,[H_4E]}$$

where $$A = 1 + \frac{1}{K_I[H_4E][Kw]}\left[\frac{[HGe][k_1]_{Ge}}{[K_I]_{Ge}} + \frac{[HGo][k_1]_{Go}}{[K_I]_{Go}}\right]$$

or $$A = 1 + \frac{1}{K_I[H_4E][Kw]}\left[\Sigma\frac{[HK]][k_1]_K}{[KI]_K}\right]$$

HK = any acid product

6. The rate falls off rapidly as the reaction proceeds. The rate fall off is predicted by the inclusion of the "A" term in the denominator of Equation 6.36. The rate decrease is attributed to the competition between the unreacted erythritol and the chelatable acid products for the ferric ion and is quantitatively dependent upon the stability constants of the mono-erythritol complex formation, the concentration of erythritol, the constants for the acid complex formation and the concentrations of the acids. The inhibitory effect was verified by a special test with initially added glyceric acid.

7. There is an initial unsteady state period. There was no explanation given for the abnormally high initial rate of oxidation at high initial erythritol concentrations, but it could possibly be due to the formation of a tri-erythritol complex, even more reactive than the di-erythritol complex.

8. The ferrous ion appears gradually if the oxygen addition ceases. The oxidation of the complex results in the reduction of the iron to the ferrous state, and the oxygen subsequently reoxidizes the iron to the ferric state. As the oxygen addition is stopped, the system becomes depleted of oxygen and ferrous ions appear.

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Notation

$[C_E]$ = The total concentration of erythritol, complexed and uncomplexed, gram moles/liter.

$[Fe]$ = Concentration of the ferric ion, gram moles/liter.

$[Fe]_e$ = Effective Iron(III) concentration.

Fe^{+++}_{OH,H_2O} = The ferric ion in aqueous solution, complexed with other species such as hydroxyl ions and water molecules.

$Fe(Ge)^{-1}$ = Glyceric acid-Iron(III) complex.

$Fe(Go)^{-1}$ = Glycolic acid-Iron(III) complex.

$[Fe(H_2E)^-]$ = Concentration of the mono-erythritol-Iron(III) complex, gram moles/liter.

$[Fe(H_2E)_2^-]$ = Concentration of the di-erythritol-Iron(III) complex attached at 1 and 2 oxygens, gram moles/liter.

$[Fe'(H_2E)_2^-]$ = Concentration of the di-erythritol-Iron(III) complex attached at 2 and 3 oxygens, gram moles/liter.

$[Fe(H_2E)_2^-]_{Total}$ = Total concentration of the di-erythritol-Iron(III) complex, gram moles/liter.

$= [Fe(H_2E)_2^-] + [Fe'(H_2E)_2^-]$

G_o = Mass flow rate, lbs./hr.-ft.^{2}

$[H_4E]$ = The concentration of uncomplexed erythritol, gram moles/liter.

HGe = Glyceric acid.

HGo = Glycolic acid.

k_b = Velocity constant for reaction at $T_b(^oC)$, hr.$^{-1}$.

k_a = Velocity constant for reaction at $T_a(^oC)$, hr.$^{-1}$.

$(k_1)_{Ge}$ = The formation constant for the mono-glyceric-Iron(III) complex.

$(k_1)_{Go}$ = The formation constant for the mono-glycolic-Iron(III) complex.

Kw = The ionization constant of water.

$[K_1]_{Go}$ = Ionization constant of glycolic acid.

$[K_1]_{Ge}$ = Ionization constant of glyceric acid.

K_1 = Equilibrium formation constant for mono-erythritol-Iron(III) complex.

K_{II} = Equilibrium formation constant for $[Fe(H_2E)_2^-]$ complex.

K'_{II} = Equilibrium formation constant for $[Fe'(H_2E)_2^-]$ complex.

$K''_{II} = K_{II} + K_{II'}$

k_1 = Velocity constant for disproportionation of $[Fe(H_2E)_2^-]$ complex, hr.$^{-1}$.

k_2 = Velocity constant for disproportionation of $[Fe'(H_2E)_2^-]$ complex, hr.$^{-1}$.

k' = Effective velocity constant for disproportionation of the di-erythritol-Iron(III) complexes, hr.$^{-1}$.

$$= \frac{k_1 K_{II} + k_2 K'_{II}}{K_{II} + K'_{II}}$$

[OH] = Hydroxyl ion concentration, gram moles/liter.

P_1 = Radical anion of glycolic acid.

P_{II} = Glycolaldehyde.

S_{I} = Radical anion of formic acid.

S_{II} = Formaldehyde.

T_{I} = Radical anion of glyceric acid.

T_{II} = Glyceraldehyde.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The homogenous catalyzed autoxidation of erythritol in basic solution was investigated. The product formation and reactant disappearance was followed by gas chromotographic analysis, and various "wet" analytical methods. The technique presented for the gas chromatographic analysis of erythritol and its reaction products can be readily applied to mannitol, a six carbon homolog of erythritol.

The following rate expression was derived, based on a mechanism involving the formation of two erythritol-iron(III) chelate compounds.

$$\frac{-\,d\,[C_E]}{d\theta} = \frac{k' K''_{II}\,[Fe]_o\,[H_4E]}{A + K''_{II}\,[H_4E]} \quad ;$$

where A is a catalyst poisoning factor that is dependent upon the amount of chelatable acid products, HK, formed in the reaction.

$$A = 1 + \frac{1}{K_I\,[H_4E][K_W]}\;\left[\;\Sigma\;\frac{[HK][k_1]_K}{[K_1]_K}\;\right]$$

The proposed mechanism qualitatively explains the experimental results of the investigation.

The three major products formed are glyceric, glycolic and formic acid. Aldehydes are present during the reaction and the presence of significant amounts of the major product, glyceric acid, will inhibit the reaction. Following are some recommendations for an extension of the investigation.

1. Restudy the mannitol reaction now that analytical methods are developed for the reaction products.

2. Determine the structure and charge of the erythritol-iron(III) complexes. The existence of the two complexes was predicted on the basis of the experimental data and of other known complexes of this type, but has not been verified experimentally.

3. Investigate methods of removing or deactivating the acids formed, to prevent inhibition of the reaction.

4. Develop the gas chromatographic technique for analysis of the methyl ester derivatives of the reaction products to eliminate some of the problems in the glyceric acid analysis.

5. Make some special tests to study further the nature of the intermediate compounds formed in the reaction.

6. Test the products of the reaction to see if they are oxidized under the conditions of the tests.

7. Determine the identity of the small amount of unidentifiable material on the chromatogram trace of the trimethylsilyl derivatives

of the reaction products. One possibility is erythronic acid which could be easily formed from erythritol or erythrose.

8. Employ the isotope effect to determine the role of the terminal hydrogens in the rate determining step. Mesotartaric acid could be treated with $LiAlD_4$ to produce terminally deutarated erythritol, if the compound isn't available commercially. If the hydrogen abstraction is the rate determining step, the rate should be one third to one sixth of the normal rate.
9. Determine the empirical rate constants for the derived expression by analog or digital methods, and optimize the production of glyceric or glycolic acid. Percise data on product distribution for a number of tests would be necessary.
10. Investigate the reaction rate as a function of oxygen concentration and uptake and study the effect of light and hydrogen perioxide on the rate.

APPENDIX A

DETAILED EXPERIMENTAL DATA

Table A-1

Oxidation of Glycerol

Run G-1

Date 1/13/65

Initial glycerol concentration (gram moles/liter)	= .259
Initial sodium hydroxide concentration (gram moles/liter)	= .860
Initial ferric chloride concentration (gram moles/liter)	= .010
Temperature, ^{o}C	= 40
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	glycerol concentration (gram moles/liter)	glycerol consumed (gram moles/liter)	sodium hydroxide (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
G-1-0	0	.259	.00	.860	.00
G-1-2	10.43	.266	.00	.902	-.042
G-1-3	10.647	-	-	.915	-.065
G-1-4	12.813	.257	.00	.931	-.0871
G-1-5	16.23	.259	.00	.912	-.052

Table A-11

Oxidation of Erythritol in the Absence of Catalyst

Run E-10

Date 5/18/66

Initial erythritol concentration (gram moles/liter)	= .0805
Initial sodium hydroxide concentration (gram moles/liter)	= .916
Temperature, ^{o}C	= 40
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-10-0	0	.0805	.00	1.0	.00
E-10-1	1.0	.0837	.00	1.04	.00
E-10-2	2.0	.0840	.00	1.043	.00
E-10-3	3.0	.0842	.00	1.045	.00
E-10-4	3.75	.0816	.00	1.015	.00

Table A-III

Helium Oxidation of Erythritol

Run E-11

Date 5/18/66

Initial erythritol concentration (gram moles/liter)	= .0966
Initial sodium hydroxide concentration (gram moles/liter)	= 1.06
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 40
Helium flow rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-11-0	.00	.0966	.00	1.06	.00
E-11-1	1.50	.0972	.00	1.07	.00
E-11-2	2.91	.0972	.00	1.071	.00
E-11-3	5.00	.0971	.00	1.07	.00

Table A-IV

Detailed Oxidation Data

Run E-12

Date 5/19/66

Initial erythritol concentration (gram moles/liter)	= .098
Initial sodium hydroxide concentration (gram moles/liter)	= 1.00
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 30
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-12-0	.00	.0980	.00	1.00	.00
E-12-1	.75	.088	.01	.985	.015
E-12-2	1.50	.0825	.0157	.975	.025
E-12-3	4.00	.0660	.0320	.920	.080

Table A-IV

Detailed Oxidation Data

Run E-13

Date 5/20/66

Initial erythritol concentration (gram moles/liter)	= .0989
Initial sodium hydroxide concentration (gram moles/liter)	= 1.00
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-13-0	.00	.0989	.00	1.0	.00
E-13-1	.75	.0719	.0270	.954	.046
E-13-2	1.50	.0648	.0341	.930	.070
E-13-3	4.00	.0305	.0684	.845	.155

Table A-IV

Detailed Oxidation Data

Run E-14

Date 5/21/66

Initial erythritol concentration (gram moles/liter)	= .0995
Initial sodium hydroxide concentration (gram moles/liter)	= 1.00
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 40
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-14-0	.00	.0995	.00	1.00	.00
E-14-1	.75	.0590	.0405	.928	.072
E-14-2	1.50	.0352	.0643	.874	.126
E-14-3	4.00	.0080	.0907	.780	.220

Table A-IV

Detailed Oxidation Data

Run E-15

Date 5/23/66

Initial erythritol concentration (gram moles/liter)	= .099
Initial sodium hydroxide concentration (gram moles/liter)	= 1.00
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 45
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-15-0	.00	.0990	.00	1.00	.00
E-15-1	.75	.0562	.0428	.902	.098
E-15-2	1.50	.0289	.0701	.842	.158
E-15-3	4.00	.0184	.0806	.820	.180

Table A-IV

Detailed Oxidation Data

Run E-16

Date 5/27/66

Initial erythritol concentration (gram moles/liter)	= .1082
Initial sodium hydroxide concentration (gram moles/liter)	= 1.00
Initial ferric chloride concentration (gram moles/liter)	= .001
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-16-0	.00	.1082	.00	1.00	.00
E-16-1	.50	.0971	.0111	.976	.024
E-16-2	1.25	.0979	.0103	.964	.036
E-16-3	2.50	.0798	.0284	.939	.061
E-16-4	4.00	.0774	.0308	.900	.100

Table A-IV

Detailed Oxidation Data

Run E-17

Date 5/28/66

Initial erythritol concentration (gram moles/liter)	= .1048
Initial sodium hydroxide concentration (gram moles/liter)	= .957
Initial ferric chloride concentration (gram moles/liter)	= .044
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.5

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-17-0	.00	.1048	.00	.957	.00
E-17-1	.50	.0922	.0126	.937	.020
E-17-2	1.25	.0761	.0287	.922	.035
E-17-3	2.50	.0606	.0442	.876	.081
E-17-4	4.00	.0547	.0501	.832	.125

Table A-IV

Detailed Oxidation Data

Run E-18

Date 5/28/66

Initial erythritol concentration (gram moles/liter)	= .1052
Initial sodium hydroxide concentration (gram moles/liter)	= .989
Initial ferric chloride concentration (gram moles/liter)	= .00
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.5

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-18-0	.00	.1052	.00	.989	.00
E-18-1	.70	.0995	.0057	.987	.002
E-18-2	2.46	.0987	.0065	.975	.014
E-18-3	4.00	.0974	.0078	.965	.024

Table A-IV

Detailed Oxidation Data

Run E-19

Date 5/28/66

Initial erythritol concentration (gram moles/liter)	= .105
Initial sodium hydroxide concentration (gram moles/liter)	= .942
Initial ferric chloride concentration (gram moles/liter)	= .015
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.5

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-19-0	.00	.105	.00	.942	.00
E-19-1	.5	.0829	.0221	.900	.042
E-19-2	1.25	.0665	.0385	.879	.063
E-19-3	2.50	.0404	.0646	.846	.096
E-19-4	3.97	.0241	.0809	.806	.136

Table A-IV

Detailed Oxidation Data

Run E-20

Date 6/11/66

Initial erythritol concentration (gram moles/liter)	= .1012
Initial sodium hydroxide concentration (gram moles/liter)	= .877
Initial ferric chloride concentration (gram moles/liter)	= .030
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.55

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-20-0	.00	.1012	.00	.877	.00
E-20-1	.50	.0800	.0212	.825	.052
E-20-2	1.25	.0559	.0453	.796	.081
E-20-3	2.50	.0414	.0598	.757	.120
E-20-4	4.00	.0412	.0600	.724	.153

Table A-IV

Detailed Oxidation Data

Run E-21

Date 6/12/66

Initial erythritol concentration (gram moles/liter)	= .101
Initial sodium hydroxide concentration (gram moles/liter)	= .946
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 5.46

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-21-0	.00	.101	.00	.946	.00
E-21-1	.50	.0861	.014	.906	.04
E-21-2	1.25	.0820	.0181	.869	.077
E-21-3	2.50	.0527	.0483	.839	.107
E-21-4	4.00	.0411	.0599	.790	.156

Table A-IV

Detailed Oxidation Data

Run E-22

Date 6/11/66

Initial erythritol concentration (gram moles/liter)	= .10
Initial sodium hydroxide concentration (gram moles/liter)	= .940
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 16.38

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-22-0	.00	.10	.00	.940	.00
E-22-1	.50	.0957	.0043	.910	.030
E-22-2	1.25	.0729	.0271	.900	.040
E-22-3	2.50	.0514	.0486	.820	.120
E-22-4	4.00	.0310	.0690	.756	.184

Table A-IV

Detailed Oxidation Data

Run E-23

Date 6/12/66

Initial erythritol concentration (gram moles/liter)	= .094
Initial sodium hydroxide concentration (gram moles/liter)	= .939
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 34.76

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-23-0	.00	.0940	.00	.939	.00
E-23-1	.50	.0839	.0101	.900	.039
E-23-2	1.25	.0690	.0250	.881	.058
E-23-3	2.50	.0454	.0486	.806	.133
E-23-4	4.00	.0305	.0635	.761	.178

Table A-IV

Detailed Oxidation Data

Run E-24

Date 6/17/66

Initial erythritol concentration (gram moles/liter)	= .0482
Initial sodium hydroxide concentration (gram moles/liter)	= .947
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= $35^{o}C$
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-24-0	.00	.0482	.00	.947	.00
E-24-1	.50	.0472	.001	.925	.022
E-24-2	1.25	.0402	.008	.898	.049
E-24-3	2.50	.0274	.0208	.884	.063
E-24-4	4.00	.0199	.0283	.870	.077

Table A-IV

Detailed Oxidation Data

Run E-25

Date 6/18/66

Initial erythritol concentration (gram moles/liter)	= .150
Initial sodium hydroxide concentration (gram moles/liter)	= .942
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-25-0	.00	.1500	.00	.942	.00
E-25-1	.50	.0954	.0546	.926	.016
E-25-2	1.25	.0779	.0721	.875	.067
E-25-3	2.50	.0576	.0924	.820	.122
E-25-4	4.00	.0437	.1063	.749	.193

Table A-IV

Detailed Oxidation Data

Run E-26

Date 6/18/66

Initial erythritol concentration (gram moles/liter)	= .20
Initial sodium hydroxide concentration (gram moles/liter)	= .945
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-26-0	.00	.20	.00	.945	.00
E-26-1	.50	.1205	.0795	.912	.033
E-26-2	1.25	.115	.088	.867	.078
E-26-3	2.50	.105	.095	.814	.131
E-26-4	4.00	.0938	.1062	.787	.158

Table A-IV

Detailed Oxidation Data

Run E-27

Date 6/19/66

Initial erythritol concentration (gram moles/liter)	= .30
Initial sodium hydroxide concentration (gram moles/liter)	= .947
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-27-0	.00	.300	.00	.947	.00
E-27-1	.50	.193	.107	.922	.025
E-27-2	1.25	.135	.165	.906	.041
E-27-3	2.50	.132	.168	.849	.098
E-27-4	4.00	.127	.173	.815	.132

Table A-IV

Detailed Oxidation Data

Run E-28

Date 7/2/66

Initial erythritol concentration (gram moles/liter)	= .1005
Initial sodium hydroxide concentration (gram moles/liter)	= 1.915
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-28-0	.00	.1005	.00	1.915	.00
E-28-1	.33	.0933	.0072	1.905	.010
E-28-2	1.00	.0752	.0253	1.870	.045
E-28-3	1.75	.0598	.0407	1.838	.077
E-28-4	3.00	.0429	.0576	1.765	.150

Table A-IV

Detailed Oxidation Data

Run E-29

Date 7/3/66

Initial erythritol concentration (gram moles/liter)	= .100
Initial sodium hydroxide concentration (gram moles/liter)	= .454
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-29-0	.00	.100	.00	.454	.00
E-29-1	.30	.0898	.0102	.444	.010
E-29-2	1.0	.0787	.0213	.403	.051
E-29-3	1.75	.0672	.0328	.386	.070
E-29-4	3.00	.0528	.0472	.333	.121

Table A-IV

Detailed Oxidation Data

Run E-30

Date 7/2/66

Initial erythritol concentration (gram moles/liter)	= .10
Initial sodium hydroxide concentration (gram moles/liter)	= .167
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.46

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-30-0	.00	.100	.00	.167	.00
E-30-1	.33	.092	.008	.154	.013
E-30-2	1.0	.0874	.0126	.165	-
E-30-3	1.75	.0824	.0176	.1215	.044
E-30-4	3.00	.0744	.0256	.1045	.0625

Table A-IV

Detailed Oxidation Data

Run E-31

Date 7/5/66

Initial erythritol concentration (gram moles/liter)	= .0989
Initial sodium hydroxide concentration (gram moles/liter)	= .00
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-31-0	.0	.0989	.00	.00	.00
E-31-1	.33	.0878	-	.00	.00
E-31-2	1.00	.0980	.0009	.00	.00
E-31-3	1.75	.0945	.0044	.00	.00
E-31-4	3.00	.1001	.00	.00	.00

Table A-IV

Detailed Oxidation Data

Run E-32

Date 7/6/66

Initial erythritol concentration (gram moles/liter)	= .100
Initial sodium hydroxide concentration (gram moles/liter)	= .919
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (Hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-32-0	.00	.100	.00	.919	.00
E-32-1	.33	.0875	.0125	.899	.020
E-32-2	1.00	.0806	.0195	.880	.039
E-32-3	1.75	.0616	.0384	.829	.090
E-32-4	3.00	.0464	.0536	.780	.139

Table A-IV

Detailed Oxidation Data

Run E-33

Date 7/8/66

Initial erythritol concentration (gram moles/liter)	= .10
Initial sodium hydroxide concentration (gram moles/liter)	= .617
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-33-0	.00	.0994	.00	.617	.00
E-33-1	.33	.0897	.0097	.609	.008
E-33-2	1.267	.0706	.0288	.567	.050
E-33-3	1.45	-	-	.543	.074
E-33-3'	2.083	.0617	.0377	-	-
E-33-4	3.0	.0457	.0537	.489	.128

Table A-IV

Detailed Oxidation Data

Run E-34

Date 7/30/66

Initial erythritol concentration (gram moles/liter)	= .0934
Initial sodium hydroxide concentration (gram moles/liter)	= .93
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-34-0	.00	-	-	.930	.00
E-34-1	.33	-	-	.916	.014
E-34-2	1.00	-	-	.880	.050
E-34-3	1.75	-	-	.847	.083
E-34-4	3.00	-	-	.772	.158

Table A-IV

Detailed Oxidation Data

Run E-37

Date 9/11/66

Initial erythritol concentration (gram moles/liter)	= .20
Initial sodium hydroxide concentration (gram moles/liter)	= .955
Initial ferric chloride concentration (gram moles/liter)	= .01
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-37-0	.00	-	-	.955	.00
E-37-1	.33	-	-	.921	.034
E-37-2	1.00	-	-	.889	.066
E-37-3	1.75	-	-	.849	.106
E-37-4	3.00	-	-	.789	.166

Table A-V

Oxidation of Erythritol in the Presence of Glyceric Acid

Run E-35

Date 9/9/66

Initial erythritol concentration (gram moles/liter)	= .135
Initial sodium hydroxide concentration (gram moles/liter)	= .994
Initial ferric chloride concentration (gram moles/liter)	= .01
Initial glyceric acid concentration (gram moles/liter)	= .08
Temperature, ^{o}C	= 35
Air rate (lbs./hr.ft.^{2})	= 21.56

Sample	Time (hrs.)	erythritol concentration (gram moles/liter)	erythritol consumed (gram moles/liter)	sodium hydroxide concentration (gram moles/liter)	sodium hydroxide consumed (gram moles/liter)
E-35-0	.00	.135	.00	.994	.00
E-35-1	.25	.1275	.0075	.989	.005
E-35-2	1.0	.1305	.0045	.987	.007
E-35-3	1.75	.1310	.0040	.984	.010
E-35-4	3.00	.1315	.0035	.969	.025

Table A-VI

Gas Chromatographic Results From

Run E-34*

Time (Hours)	.00		.33		1.0		1.75		3.0		
Component	Φ	Conc. M	Φ	Conc. M	Φ	Conc. M	Φ	Conc. M	Φ	Conc. M	K Used
Erythritol	2.33	.0934	1.848	.0736	1.32	.0528	.964	.0385	.871	.0349	.382
Glyceric Acid #1	.00	.00	.0117	.00404	.0196	.000677	.0494	.001705	.322	.0111	.33
Glyceric Acid #2	.00	.00	.10	.00745	.274	.0204	.368	.0274	.800	.0595	.71
Total Glyceric Acid		.00		.00785		.0211		.0291		.0706	
Glycolic Acid	.00	.00	.00	.00	.085	.00286	-	-	.1519	.0051	.321
Lactic Acid	.00	.00	.05	.00157	.046	.00144	.062	.00194	.0278	.000872	.30

* Initial ferric chloride concentration = .01M

Temperature = 35°C

Air flow rate = 21.56 lbs./hr.ft.^{2}

Reagent dosage = 1 ml. "tri-sil", .3 ml. .03 grams/ml. diphenyl and .3 ml. .015 grams/ml. diphenyl added to .834 mls. of the product solution.

Table A-VII

Gas Chromatographic Results From

Run E-37*

Time (Hours)	.00		.33		1.0		1.75		3.0		
Component	Φ	Conc. M	Φ	Conc. M	Φ	Conc. M	Φ	Conc. M	Φ	Conc. M	K Used
Erythritol	1.675	.20	1.508	.18	1.25	.149	1.03	.123	.971	.116	-
Glyceric Acid #1	.00	.00	.0387	.00216	.0919	.00527	.1445	.00836	.408	.0235	.33
Glyceric Acid #2	.00	.00	.064	.00795	.156	.01935	.226	.0287	.380	.0472	.71
Total Glyceric Acid		.00		.01011		.0246		.03647		.0707	
Glycolic Acid	.00	.00	.0533	.00298	.3367	.0188	.290	.0162	1.014	.0567	.321
Lactic Acid	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	-

* Initial ferric chloride concentration = .01M

Temperature = 35°C

Air flow rate = 21.56 lbs./hr.ft.^{2}

Reagent dosage = 5.0 mls. "tri-sil" and 1.5 mls. .03 grams/ml. diphenyl added to 1.669 mls. of product solution.

APPENDIX B

SAMPLE CALCULATIONS AND EXPERIMENTAL PROCEDURE

A. Sample Calculation for Periodic Acid Analysis

(See Chapter IV for a discussion of the method.)

Run E-21 Sample 1

thiosulfate required for blank = 100.00 mls.

thiosulfate required for sample = 82.46 mls.

From Equations 3.1, 3.2 and 3.3, the amount of free iodine is reduced by 3 moles for every mole of erythritol reacted. The free iodine is titrated by standard sodium thiosulfate.

$$I_2 + 2\ Na_2S_2O_3 \rightarrow 2I^- + Na_2S_4O_6$$

The concentration of erythritol is thus:

$$\frac{\text{Conc. gram moles}}{\text{Liter}} = \frac{[(\text{Ml. thio for Blank}) - (\text{Ml. thio for Sample})]\ N_{Thio}}{3 \times 2 \times (\text{Ml. of Sample})}$$

$$N_{Thio} = .294$$

For Sample E-21-1

$$\text{Conc.} = \frac{(100-82.46)\ (.294)}{3 \times 2 \times 10} = \frac{.0860 \text{ gram moles erythritol}}{\text{Liter}}$$

B. Control Tests

Various control tests were made to ensure that the resins would take out the acids present, and would not remove any charged complex that contained erythritol.

Test #1

10 ml. samples of .1069 molar glyceric acid were treated with Amberlite IR-400 anion exchange resin in a 10 mm. x 250 mm. packed column. The flow rate was 4 mls./min. The flow rate recommended by the Amberlite Laboratory Guide is 2-4 mls./min. The higher flow rate and the high acid concentration were tested to determine the error resulting from the worst possible conditions. The resin took out 79.8% of the glyceric acid. At a lower flow rate and at lower acid concentration the efficiency would probably be greater. Most of the runs were made at conditions under which the glyceric acid concentration did not exceed .05 molar. Possibly one of the runs that would have the maximum error is run E-26 in which the glyceric acid concentration is probably about .08M. Using the efficiency calculated above, the erythritol equivalent of glyceric acid, and the fraction of glyceric acid that reacts with periodic acid in 1.5 hours, the maximum percent error in the erythritol concentration would be about 8 percent.

erythritol present = .096M

$$\text{Percent error} = \frac{.08 \times .202 \times .72 \times .667}{.096} \times 100 = 8.04$$

Test #2

Another test was made in which the 10 ml. sample was diluted to 30 mls. and the flow rate reduced to 2 mls. per minute. Under these conditions the resin removed 86.71% of the acid. Calculating the maximum error from run E-26 as before

$$\text{Percent error} = \frac{.08 \times .1329 \times .72 \times .667}{.096} = 5.27$$

At his initial erythritol concentration the error may become significant in the latter parts of a run.

Test #3

An ion exchange test was made of a synthetic solution containing .053 moles/liter erythritol, .01 moles/liter ferric chloride, 1.0 moles/liter sodium hydroxide, and .0637 moles/liter glyceric acid. The ion exchange product was nearly neutral and analyzed as .0516 moles/liter erythritol. The original solution analyzed as .085 moles/liter erythritol. The 10 ml. sample was diluted to 30 mls. and treated in series with IR-120 and IR-400 with a flow rate of 2.0 mls./min.

Test #4

As described in Chapter V, direct treatment of the complex solution with an anion exchange resin resulted in removal of

part of the erythritol as a complex. Tests showed that primary treatment of the complex with a cation exchange resin would remove only the iron. The final procedure selected was to first break the complex by treating with the cation exchange resins, followed by treatment with an anion exchange resin to remove the acids. After treatment with the resins the sample is oxidized with periodic acid as outlined in Appendix A. The ion exchange procedure is listed below.

Ion Exchange Procedure

1. A ten ml. sample is introduced into an extraction flask connected to a 10 mm. ID x 300 mm. chromatographic tube (manufactured by Corning Glass). Figure (B-1) is a sketch of the apparatus. The tube is packed to a height of 250 mm. with Amberlite IR-120 cation exchange resin.
2. The outlet of the chromatographic tube is connected by tygon tubing to another tube in series that is packed with Amberlite IR-400 anion exchange resin.
3. The flow rate is adjusted to 2 mls. per minute. The flow rate is suggested by the Amberlite Laboratory Guide and is approximately .1 bed volumes per minute.
4. The resins are washed with 60 ml. of distilled water.
5. The IR-120 and IR-400 are regenerated by hydrochloric acid and sodium hydroxide respectively. The Amberlite IR-400 is manufactured by Mallinckrodt Chemical Company and is only

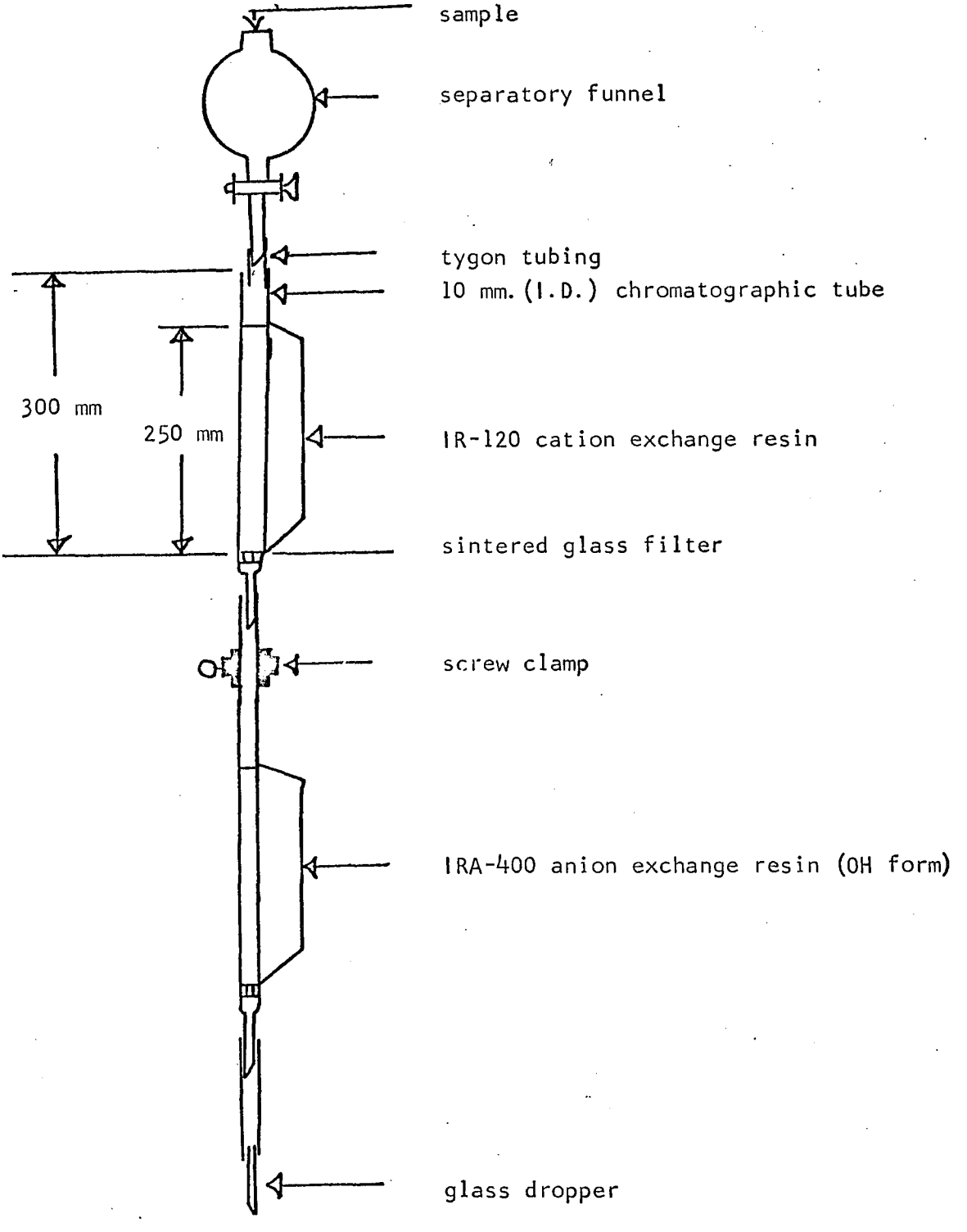

Figure (B-1)

Schematic diagram of the ion exchange apparatus.

available in the CL^- form. The resin is converted to the OH^- form with sodium hydroxide. The regeneration rate used was also 2 mls. per minute.

C. Analysis of Formic Acid and Carbon Dioxide

Reid and Weihe[7] have stated that oxalic acid, glycerol, lactic acid and acetaldehyde would not interfer with the mercuric acetate test for formic acid. Glyceric acid was also tested for interference and several samples of formic acid were analyzed for control purposes.

Sample	Concentration of Acid Gram moles/liter	Results of Mercuric Acetate Test For Formic Acid Gram moles/liter
Formic Acid	.04	.0407
Formic Acid	.04	.0408
Glyceric Acid	.10	.00
Formic	.25	.252

The procedure used is essentially that of Reid and Weihe and is summarized below. (See Figure (IV-11).)

1. A ten ml. aliquot of the sample is acidified with HCL. (25 percent in excess of that required for neutralization).

2. The solution is purged with air, scrubbed free of CO_2 by ascarite, and passed through three gas washing bottles in series,

connected to a vacuum. The bottles are filled with freshly filtered barium hydroxide.

3. The solution is gently heated until no barium carbonate is precipitated from a fresh bottle of barium hydroxide. The barium carbonate is filtered through porous alundum filtering crucibles. The crucibles used are 35 ml., coarse RA98 Sargent Crucibles. The crucibles are heated to a constant weight, freed from barium carbonate with acetic acid, heated and reweighed. The conc. of carbon dioxide is proportional to the precipitated barium carbonate.

4. 10 ml. of .313 m. mercuric acetate is added slowly to the solution.

5. The solution is boiled gently for 30 minutes and the barium carbonate is recovered as in step 3.

$$\text{Conc. carbon dioxide, } \frac{\text{Gram moles}}{\text{Liter}} = \frac{\frac{(\text{wt } BACO_3, \text{ Step 3})}{197.37}}{\frac{\text{Ml. Sample}}{1000}}$$

$$\text{Conc. formic acid, } \frac{\text{Gram moles}}{\text{Liter}} = \frac{\frac{(\text{wt } BACO_3, \text{ Step 5})}{197.37}}{\frac{\text{Ml. Sample}}{1000}}$$

D. Spot Tests

Several spot tests were made for aldehydes and the various acids.

The tests were all taken from Feigl.[2] The procedures and reagents used are summarized below.

1. Formaldehyde - Chromatropic acid test[3]. The solution is heated with 1.8 - dihydroxynaphtalene - 3,6 - disulfonic acid in strong sulfuric acid solution. A violet-pink color appears in the presence of formaldehyde.

2. Formic Acid - Formic acid is reduced to formaldehyde by magnesium and hydrochloric acid. The chromatropic acid test is then repeated. Glucose interferes but no other sugars or acids do.

3. Oxalic Acid - Oxalic acid is melted[4] with diphenylamine and aniline blue is produced. Formic, tartartic, glycolic and glyoxylic acid do not interfere.

4. Lactic Acid - Lactic acid is treated with concentrated sulfuric acid to produce acetaldehyde.[5] The acetaldehyde is identified by a color reaction with p-hydroxydiphenyl forming a deep violet color.

5. Glyceric Acid - Glyceric acid[6] produces a blue color when an aqueous solution is heated with sulfuric acid in which a little naphthoresorcinol has been added.

6. Aldehydes - Colored schiffs bases are produced when aldehydes are reacted with O-dianisidine. Tables are given in Feigl[7] that list the colors formed and the limits of identification.

Literature Cited

1. Amberlite Ion Exchange Resins, Laboratory Guide, Mallinckrodt Chemical Works, St. Louis, Missouri.
2. Feigl, F., Qualitative Analysis by Spot Tests, Elseview Publishing Company, Inc., New York, 1946.
3. Ibid., page 395.
4. Ibid., page 403.
5. Ibid., page 400.
6. Ibid., page 401.
7. Reid, J. David and Weihe, Herman D., Industrial and Engineering Chemistry, Analytical Edition, Vol. 10, No. 5, 1938.
8. Vogel, Arthur I., Elementary Practical Organic Chemistry, Part III, Quantitative Organic Analysis. 1st ed. Longmans, Green and Co., New York: 1958. pp. 680-685.

APPENDIX C

CALIBRATION CURVES

Figure C-I is a calibration curve for the temperature control system described in Chapter III, and Figure C-II gives the calibration values for the rotameter used for air flow control.

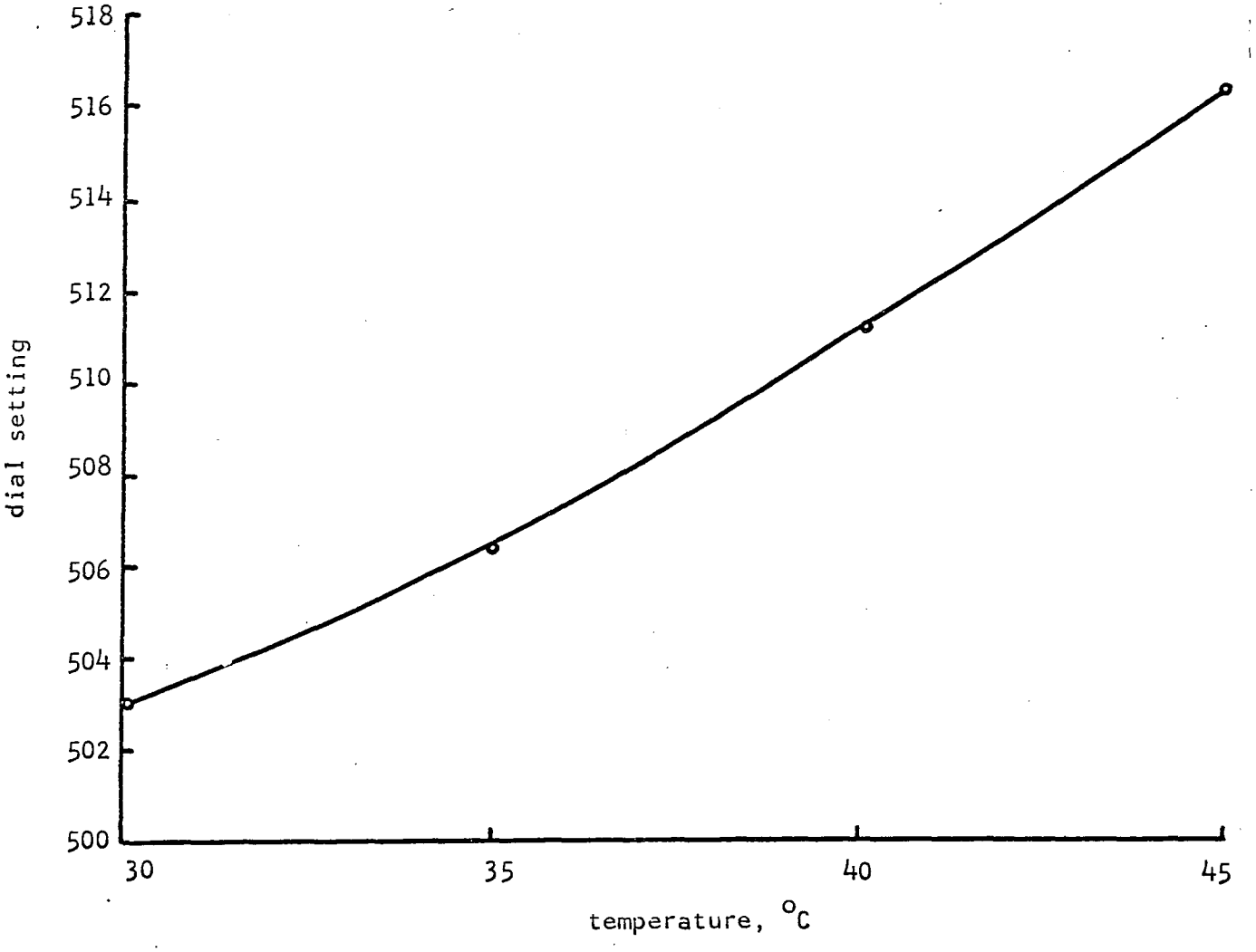

Figure (C-1)

Calibration curve for temperature control system.

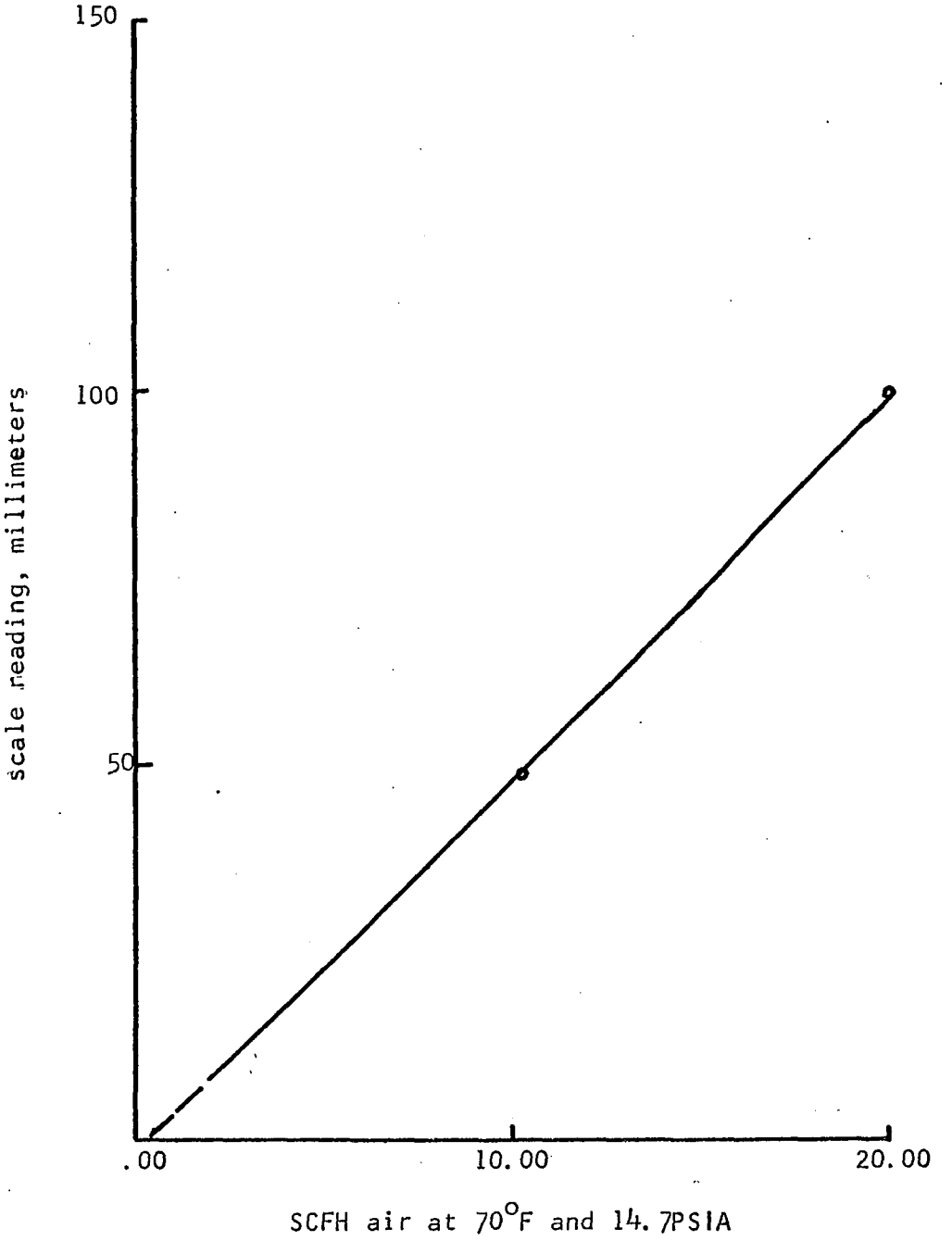

Figure (C-11)

Rotameter calibration curve.

APPENDIX D

CALIBRATION OF GAS CHROMATOGRAPH

In gas chromatography, a sample is injected into a vaporizer and then swept into a packed column by a carrier gas. Separation of components is then effected by absorption, chemical bonding, and filtration forces on the individual molecules. The emerging gases then pass through a detector that records the components as a series of peaks. The detector response may be due to the difference in thermal conductivity of the carrier gas and the sample or as is the case with the hydrogen flame detector, the sample may be ionized by combustion. The area under the peak is proportional to the amount of material in the sample. Each compound gives a characteristic response so that a calibration curve must be constructed. The absolute area under the curve also may vary for a single component due to changes in detector current or combustion gas flow rate. An internal standard is therefore added to each sample and the calibration is made with respect to the standard. In the present work diphenyl was chosen as the internal standard because of it's sharp response and location on the chromatogram trace.

A. Product Calibration

Known weights of the pure components were mixed with "Tri-Sil"*

---

* The composition of Tri-Sil is described in Chapter IV.

and a measured amount of diphenyl. Calibration constants were determined by the following relationship.

$$\left(\frac{C_{Sample}}{C_{Diphenyl}} \right) = K \, \Phi \qquad D.1$$

where C_{Sample} = concentration of unknown component in the "tri-sil" solution $\frac{\text{gram moles}}{\text{liter}}$

Φ = area ratio = $\frac{\text{area of pure sample peak}}{\text{area of diphenyl peak}}$

K = an experimentally determined calibration constant.

The areas were determined by a compensating polar planimeter manufactured by Keuffel and Esser Co. (Model 620000).

The concentration of the component in the solution was then related to concentration in the tri-sil solution by the following formula.

$$C_{Solution} = C_{Sample} \times \frac{\text{mls. "tri-sil"}}{\text{mls. original solution}} \qquad D.2$$

The following sections contain the calibration constants for various hydroxy compounds. Since the "constant" K sometimes varys with the concentration, K was calculated at various values. The calibration method used is similar to the one presented by Smith.[1]

B. Calibration Curves for Thermal Conductivity Cell

Figures (D-I) and (D-II) contain the calibration curves for various hydroxy compounds. The conditions for the runs are tabulated in Table (D-I).

C. Calibration Curves for Hydrogen Flame Detector

The standard conditions for the analysis are tabulated in Table (D-II). The calibration curves for the product compounds are shown in Figure (D-III).

D. Product Distributions - Sample Calculations

Tables (A-VI) and (A-VII) give the results from gas chromatographic tests of two runs, E-34 and E-37.

Sample Calculation Run E-37-2 1.0 hours

For glyceric acid there are two peaks; each peak has been calibrated separately.

Peak #1

Conc. diphenyl = $.0449 \frac{\text{moles}}{\text{liter}}$

Φ = .0919 (area ratio) Table (A-VII) (measured from chromatagram trace)

K = .33 (calibration constant) Figure (D-II)

$$\left(\frac{C_{Sample}}{.0449}\right) = .33\ (.0919)$$

$$C_{Sample} = .0449 \times .33 \times .0919 = .00144\underline{M}$$

$$C_{Solution} = C_{Sample} \times \frac{\text{ml. tri-sil}}{\text{ml. sample}} = .00144\underline{M} \times \frac{6.5}{1.67} = .0056\underline{M}$$

Peak #2

$\Phi = .156$

$K = .957$

$$\frac{C_{Sample}}{.0449} = .957\ (.156)$$

$$C_{Sample} = .00645\underline{M}$$

$$C_{Solution} = .00645 \times \frac{6.5}{1.67} = .026\underline{M}$$

Total Conc. glyceric acid = $.0056\underline{M} + .026\underline{M} = .0316\underline{M}$

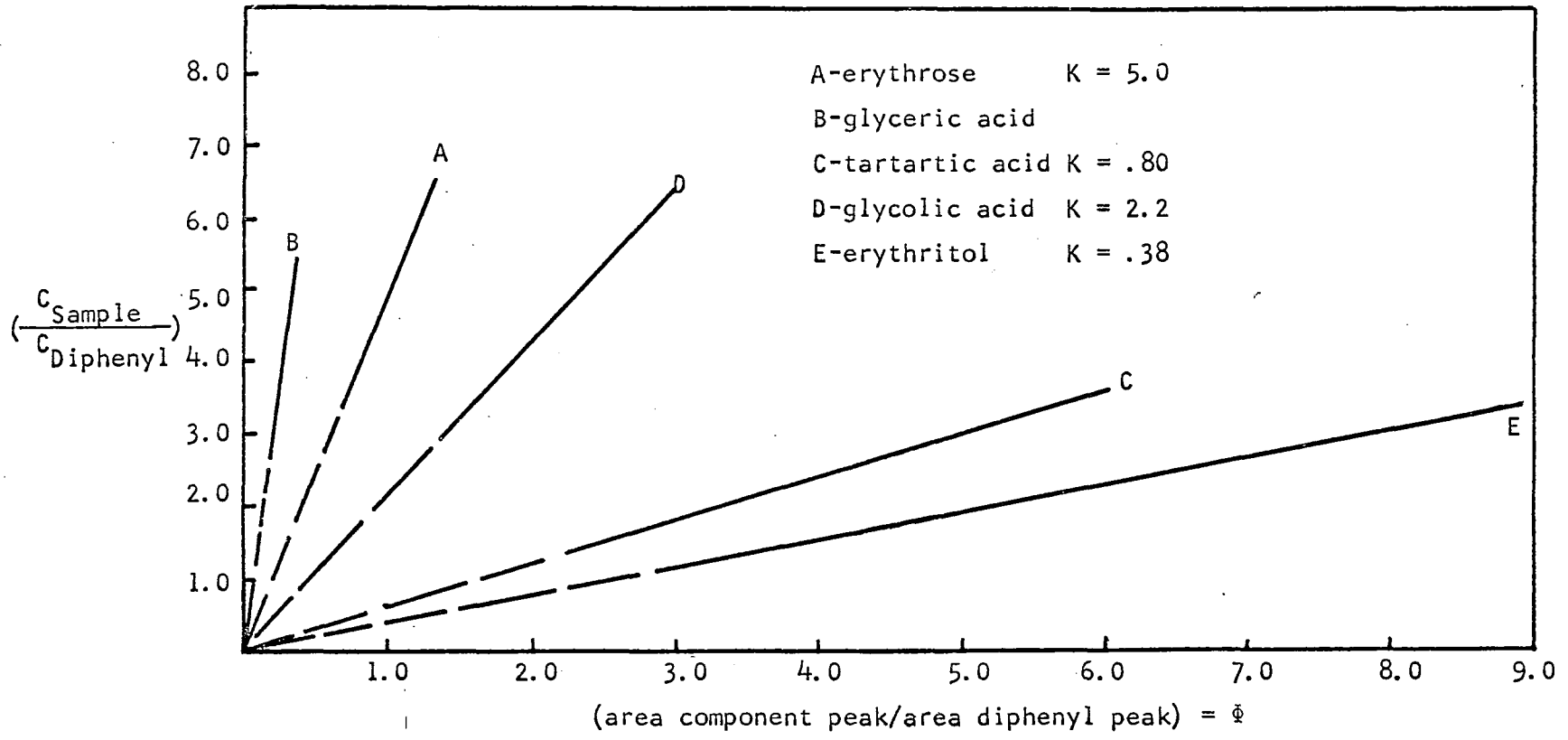

Figure (D-1)

Calibration curves for various hydroxy compounds using the thermal conductivity detector.

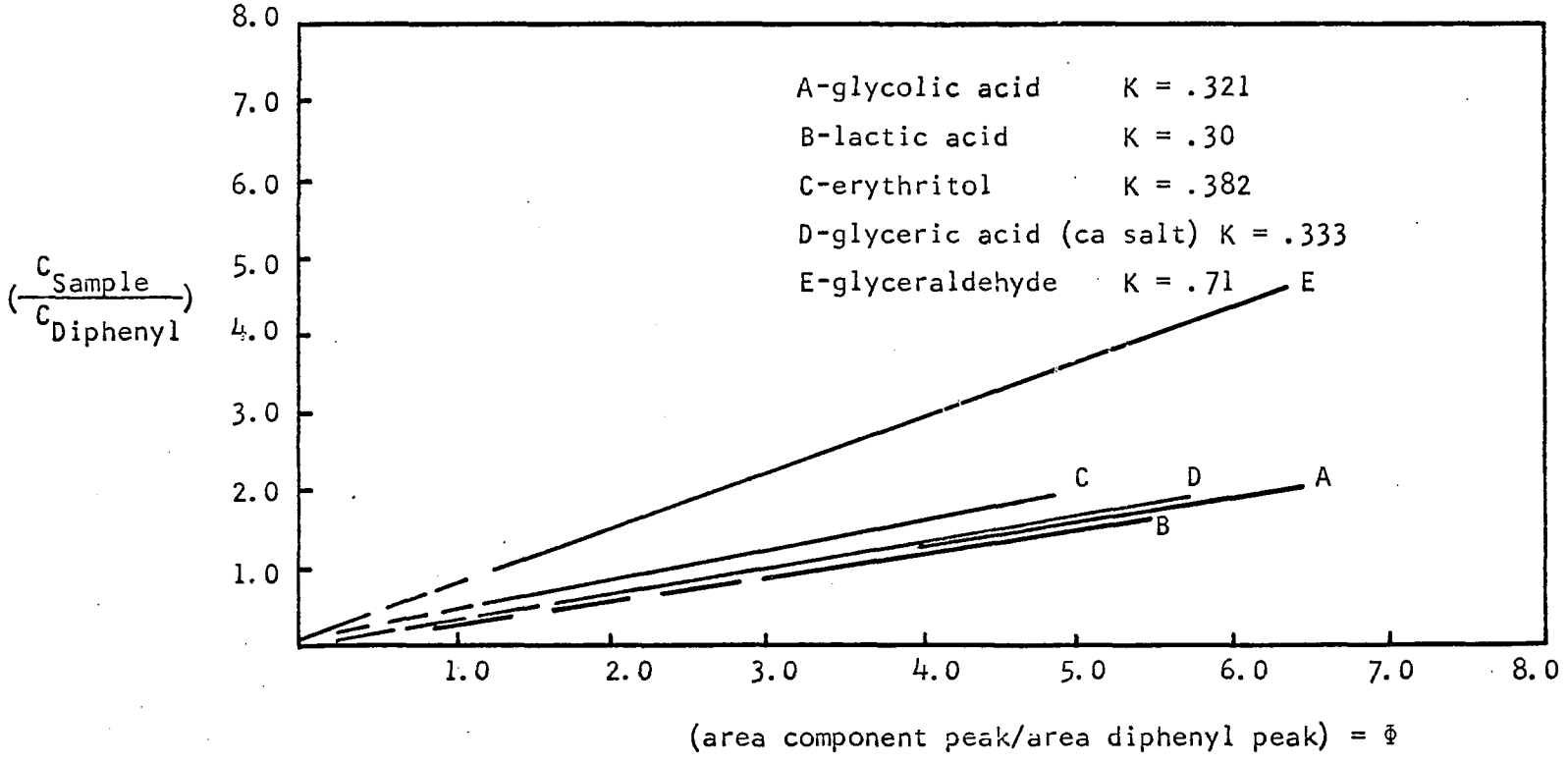

Figure (D-11)

Calibration curves for the reaction products using the hydrogen flame ionization detector.

Table (D-1)

Standard Conditions for G.C. Analysis Using
the Thermal Conductivity Detector

Instrument - Micro Tek G.C. 2500R

Detector - Thermal conductivity

Detector temperature - 260°C

Bridge current - 600 ma.

Column = 2" x 1/4" S.S. 5% SE-30 on 80/100 chromport T

Column temperature - 60°C (3 minutes) - 225°C

Temperature progression rate - 10°C/min.

Carrier gas - helium - grade A - prepurified

Carrier gas flow rate - 59 cc./min. (column #1), 43 cc./min. (column #2)

Carrier gas pressure - 30 PSIG

Sample size - 2-4 μL

Attentuation - 2-4

Recorder - Honeywell "Electronik 15"

Chart speed - 2"/min.

Syringe - Hamilton 701, 0-10 μL

Heater Settings

Oven	Setting	Temperature °C
Inlet block	53	270°
Outlet block	51	270°
Valve oven	79	120°
Thermal conductivity cell	530	240°
Column heater	413	60°

Table (D-11)

Standard Conditions for G.C. Analysis Using the Hydrogen Flame Detector

Instrument - Micro Tek G.C. 2500R

Detector - Single flame ionization detector

Hydrogen flow rate - 60 cc./min.

Hydrogen pressure - 20 PSIG

Air flow rate - .6 cubic feet/hour

Air pressure - 20 PSIG

Column - 6' x 1/8" S.S. 1% neopentyl glycol succinate and 2% SE-30 on J.M. H.P. chromsorb W 100/120

Column temperature - 60°C (3 minutes) - 225°C

Temperature progression rate - 14°C/min.

Carrier gas - helium - grade A - prepurified

Carrier gas flow rate - Column #1 - 10 cc./min., Column #2 - 26 cc./min. (Column #2 is the sample column)

Carrier gas pressure - 30 PSIG

Sample size - .3 to 1.0 μL

Attentuation - 10^2 x 2 and 10^2 x 4

Recorder - Honeywell "Electronik 15"

Chart speed - 2"/min.

Syringe - Hamilton #7001-N, 0-1 μL

Heater Settings

Oven	Setting	Temperature °C
Ionization heater	86	270°
Inlet block	53	270°
Outlet block	51	270°
Valve oven	79	120°
Column heater	413	60°

Literature Cited

1. Smith, Bengt and Carlsson, Acta Chemica Scand. 17 (1963), 455-460.

Notation

C_{Sample} = concentration in the "tri-sil" solution., gram moles/liter.

$C_{Solution}$ = concentration in the original aqueous solution., gram moles/liter.

K = an experimentally determined calibration constant.

μL = micro liter, 10^{-6} liters

Φ = area ratio, $\frac{\text{area of sample peak}}{\text{area of diphenyl peak}}$

APPENDIX E

REAGENTS

1. Amberlite IR-120, analytical reagent, strongly acidic, sulfonated polystyrene, cation exchange resin; medium porosity. Mallinkrodt Chemical Company.

2. Amberlite IR-400 C.P., strongly basic, Quaternary Ammonium (Polystyrene) Type (aminated with trimethyl amine), anion exchange resin-medium porosity, Mallinckrodt Chemical Works.

3. Ascarite, 20-30 mesh, Arthur H. Thomas Company.

4. Periodic acid, reagent grade, manufactured by G. Fredrick Smith. .10N as monobasic acid. Dissolve 22 grams of pure periodic acid in 1000 ml. distilled water.

5. Potassium iodide. Fischer Scientific Company, certified reagent.

6. Sodium thiosulfate. .2N dissolve 400 grams of sodium thiosulfate pentahydrate in 8 liters of freshly boiled distilled water. The sodium thiosulfate was standardized by potassium iodate standard ampules purchases from Anachemia Chemicals Ltd. The sodium thiosulfate is Fisher certified reagent grade.

7. Barium hydroxide, 4 oz. Fisher certified reagent, Fisher Scientific Company.

8. Mercuric acetate, 1/4th lb., analytical reagent, Mallinckrodt Chemical Works.

9. 1.8 - dihydroxynaphalene - 3,6 disulfonic acid. Disodium salt, practical, 100 grams, Eastman Organic Chemicals.

10. O-diphenylamine, practical, Matheson Coleman and Bell.

11. P-hydroxyldiphenyl, 500 grams, Matheson Coleman and Bell.

12. Naphtharesorcinol, purified, Fisher Scientific Company.

13. O-dianisidine (3,3' - dimethoxybenzidine) 100 grams, Eastman Organic Chemicals.

14. "Tri-Sil", reagent formulation for rapidly producing thrimethylsilyl derivatives of polar compounds for gas chromatography, Pierce Chemical Company.

15. Diphenyl, 250 grams, Matheson Coleman and Bell, standard solution, .03 grams/ml. diphenyl in reagent grade pyridine.

16. i-erythritol, 100 grams, recrystallized twice, Nutritional Biochemicals Corporation.

17. DL-glyceric acid (Ca salt) dihydrate, 5 grams, Sigma Chemical Company.

18. Glyceric acid - purchased as 65% aqueous solution, 25 grams, Aldrich Chemical Company.

19. Glycolic acid, 10 grams, K & K Laboratories.

20. Tartronic acid, 10 grams, Nutritional Biochemicals Corporation.

21. Glyoxylic acid, 250 mg., Calbiochem.

22. DL-glyceraldehyde, 5 grams, Nutritional Biochemicals Corporation.

23. Ferric chloride, $FeCL_3,6H_2O$, Fisher certified reagent, Fisher Scientific Company.

24. Tartartic acid, 4 oz. reagent grade, B & A Chemicals.

APPENDIX F

CALCULATION OF EFFECTIVE VELOCITY CONSTANT, k'

$$\frac{-d\,C_E}{d\theta} = k_1\,[Fe(H_2E)_2^-]_{II} + k_2\,[Fe'(H_2E)_2^-]_{II'} \qquad 6.9$$

we know that:

$$K_{II} = \frac{[Fe(H_2E)_2^-]}{[H_4E][Fe(H_2E)^-]} \qquad 6.7$$

$$K_{II'} = \frac{[Fe'(H_2E)_2^-]}{[H_4E][Fe(H_2E)^-]} \qquad 6.8$$

Dividing 6.7 by 6.8

$$\frac{[Fe(H_2E)_2^-]}{[Fe'(H_2E)_2^-]} = \frac{K_{II}}{K'_{II}} \qquad F.1$$

Defining $[Fe(H_2E)_2^-]_{Total}$ as follows:

$$[Fe(H_2E)_2^-] + [Fe'(H_2E)_2^-] = [Fe(H_2E)_2^-]_{Total} \qquad F.2$$

Substituting F.1 into F.2

$$[Fe'(H_2E)_2^-] \frac{K_I}{K_{I'}} + [Fe'(H_2E)_2^-] = [Fe(H_2E)_2^-]_{Total} \qquad F.3$$

$$\therefore$$

$$[Fe'(H_2E)_2^-]_{II'} = [Fe(H_2E)_2^-]_{Total} \times \frac{K_{II'}}{K_{II} + K_{II'}} \qquad F.4$$

likewise

$$[Fe(H_2E)_2^-]_{II} = [Fe(H_2E)_2^-]_{Total} \times \frac{K_I}{K_I + K_{I'}} \qquad F.5$$

Substituting Equations F.4 and F.5 into 6.9 and combining the coefficients

$$\frac{-d\,[C_E]}{d\theta} = k'\,[Fe(H_2E)_2^-]_{Total}$$

where

$$k' = \left(\frac{k_I K_{II} + k_2 K_{II'}}{K_{II} + K_{II'}} \right)$$

AUTOBIOGRAPHY

Kenneth Charles Scott was born on October 15, 1940, in Paducah, Kentucky. He attended elementary and secondary schools at West Paducah, Kentucky, graduating from Heath High School in 1958. He attended Paducah Junior College in Paducah, Kentucky, Murray State University in Murray, Kentucky, and the University of Missouri School of Mines and Metallurgy in Rolla, Missouri and graduated cum Laude, with a Bachelor of Science Degree in Chemical Engineering in August, 1962. He enrolled in graduate school at Louisiana State University and received a Master of Science Degree in Chemical Engineering.

He was employed for summer work by B. F. Goodrich Chemical Company (2 summers), Union Carbide Nuclear Company (2 summers), Kaiser Aluminum Company and Ethyl Corporation (2 summers). In the summer of 1966 he was employed as a 1/2 time Instructor in the Department of Chemical Engineering, Louisiana State University. He has accepted employment with the Research and Development Department of the Olefins Division of Union Carbide Corporation. In 1962, he married the former Paula Schneider and is the father of one child. He is presently a candidate for the degree of Doctor of Philosophy in the Department of Chemical Engineering.

EXAMINATION AND THESIS REPORT

Candidate: Kenneth Charles Scott

Major Field: Chemical Engineering

Title of Thesis: Kinetics of the Catalytic Autoxidation of Erythritol in Basic Solution

Approved:

F. R. Groves Jr.
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Eugene W. Berg

Jesse Coates

Date of Examination:

October 31, 1966